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ENHANCING THE EFFICACY OF LOW-PRESSURE MEMBRANES FOR MICROBIAL REMOVAL

BY

KHOSROW FARAHBAKHSH ©

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN

PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

ENVIRONMENTAL ENGINEERING

DEPARTMENT OF CIVIL & ENVIRONMENTAL ENGINEERING

EDMONTON, ALBERTA

Fall 2003

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The undersigned certify that they have read, and recommended to the faculty of Graduate Studies and Research, for acceptance, a thesis entitled: ENHANCING THE EFFICACY OF LOW-PRESSURE MEMBRANES FOR MICROBIAL REMOVAL submitted by: Khosrow Farahbakhsh in partial fulfillment of the requirement for the degree of DOCTOR OF PHILOSOPHY IN ENVIRONMENTAL ENGINEERING.

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DEDICATION

This work is dedicated to my Bahá'í sisters and brothers in Iran who have been, for over two decades, deprived of their basic human rights, including the right to pursue post-secondary education. It is to their sacrifices and their steadfastness that this thesis is dedicated.

ABSTRACT

The focus of this research project was to address two outstanding issues with respect to microbial removal efficiency of low-pressure membranes; integrity monitoring and virus removal. The impact of air diffusion through intact pores on the pressure decay test was investigated. It was shown that between 34 and 103 kPa (5 and 15 psi) air diffusion through an intact wetted membrane can be described by Fick's first law of diffusion, as long as the impact of pore tortuosity, porosity, and the effective length of diffusion path is accounted for. To this end, a new parameter, referred to as the membrane parameter (κ,), was defined and successfully measured for the ZW500d© membrane. Using this new parameter and the Fick's first law of diffusion, diffusive air flow rate for the intact ZW500d© membrane and its contribution to pressure decay rate was closely estimated. It was also shown that water temperature can have a significant impact on the diffusive air flow rate and pressure decay rate through an intact membrane with the largest impact at near zero degree (approximately 40% reduction in pressure decay rates). It was also shown that submergence and the extent of membrane fouling also impacts the rate of diffusion and pressure decay of an intact membrane. In addition, the pressure decay test was validated through challenge studies, using spores of *Bacillus megaterium* for two membrane pilot plants, ZW500d© and ZW1000©. The impact of backpulsing on the log removal values for a compromised membrane was also investigated. The application of latex microspheres, as surrogates for *Cryptosporidium* spp., in membrane challenge studies was also investigated. It was shown that 0.5 μm yellow green or yellow orange fluorescent beads were the most suitable surrogates and confocal laser scanning microscopy was the most promising method of enumerating latex beads in permeate samples. Two mechanisms were proposed for the rejection of bacteriophages by microfiltration membranes. These mechanisms were adsorption to the pores and surface for a clean membrane and removal by the fouling layer for a fouled membrane. Membrane fouling was shown to markedly increase bacteriophage removal. Solution pH was found to have a significant impact on inactivation of bacteriophages and coagulation was shown to improve bacteriophage rejection by a clean membrane. Chemical coagulation was also shown to be effective in improving the performance of a low-pressure membrane by retarding the rate of membrane fouling.

ACKNOWLEDGMENTS

This work owes much of its success to the unselfish effort of many individuals and support from several institutions. Foremost among them is my friend and supervisor, Dr. Daniel W. Smith whose continual support and encouragement was a major driving force at the times when little light could be discerned in the winding tunnel of research. I particularly appreciated Dr. Smith's willingness to allow me to develop my own area of expertise without unnecessary interference. Yet he was always ready and willing to lend a hand, to discuss ideas, to provide guidance, and to facilitate further learning by providing the means for involvement with interesting projects and attending seminars and conferences. My life's partner and beloved wife, Rachel, is another individual to whom I owe much of my success. Rachel selflessly carried the brunt of raising three children in a small and cramped University residence allowing me to devote time to my research, always cheerful, never complaining or demanding. I could accomplish little without drawing on her strength and her invigorating spirit. My children; Carmel, Isaiah, and Mona, whom I love deeply, allowed me, with much understanding and love, to be a part-time father, to escape my storytelling duties and to be in my office when they needed fatherly lullabies. I am deeply grateful for their generous spirits. My friends and colleagues, Rodney Guest and Clark Svrcek, have been a constant source of support and encouragement throughout my research. Through many though provoking discussions, running errands, helping with laboratory setup, doing laborious analytical work and collecting data, they have always been there for me as only true friends would.

I also wish to acknowledge financial support provided by the Natural Science and Engineering Research Council of Canada through their Collaborative Research and Development Grant. Support of Zenon Environmental Inc., by providing equipment and technical support, as well as financial support is also greatly appreciated. In particular, I wish to thank Dr. Pierre Côté for his valuable guidance and input throughout the project as well as Dr. Nicholas Adam for his contributions to the project. The financial support from EPCOR and City of Edmonton is also appreciated.

I would also wish to thank the staff of the Environmental Engineering Program, Mr. Nick Chernuka, Ms. Debra Long, Ms. Maria Demeter, and Mr. Gary Solonynko for their assistance during my PhD work. The valuable assistance of Mr. Steve Pickles towards the end of this project is also appreciated. Other individuals who I wish to thank for their advice and assistance are Dr. Mohamed Gamal El-Din, Dr. Steve Craik, and Dr. Ian Buchanan of the Environmental Engineering Program and Mr. Geoff Heise from the Gold Bar Wastewater Water Treatment Plant.

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LIST OF SYMBOLS

A	membrane's surface area (m^2)
$C_1 - C_0$	concentration gradient for air across the wetted membrane ($mol.m^{-3}$)
CF	concentration factor
d	diameter of the largest pore (m)
d	diameter of microspheres (μm)
D	diffusivity constant for air-water system, ($m^2.s^{-1}$)
$D_{f\text{-}water}$	diffusion coefficient of the gas component-water system ($m^2.s^{-1}$)
$D_{(To,Po)}$	diffusion coefficient at 25°C and 1 atm ($m^2.s^{-1}$)
$D_{O2\text{-}H2O}$	diffusion coefficient of oxygen in water ($m^2.s^{-1}$)
f_1	air-to-water conversion factor
f_2	transmembrane pressure conversion factor
g	acceleration of gravity ($m^2.s^{-1}$)
gfd	USgal $ft^{-2}d^{-1}$
h	height of capillary rise (m)
H	Henry's constant ($mol.atm^{-1}.m^{-3}$)
J_{SP}	Specific flux (ratio of flux to TMP) ($Lm^{-2}h^{-1}kPa^{-1}$)
k	the correction factor for the shape of the largest pore
L	length of diffusive path (m)
LRV	log removal values
LRV_{max}	maximum log removal value that can be verified by a direct integrity test

M_{H2O}	molecular weight of water (g/mol)
N	molar flux of diffused air per unit area and unit time ($mol.s^{-1}$)
N	number of microspheres per mL of suspension
P_1	applied test pressure (atm)
P_0	downstream pressure (atm)
P_B	the bubble point pressure (Pa)
P_i	initial test pressure (atm)
P_f	final test pressure (atm)
PDR	pressure decay rate for a given membrane, ($atm.min^{-1}$)
P_{atm}	atmospheric pressure (kPa)
P_{test}	test air pressure (kPa)
P_{filt}	transmembrane pressure (kPa)
$\Delta P/t$	pressure decay rate ($kPa.min^{-1}$)
Q_{Breach}	total flow from the smallest breach that can be detected by a direct test
$Q_{diffusion}$	diffusion rate of air in water
Q_{filt}	filtrate flow rate ($L.min^{-1}$)
Q_{DAF}	air flow rate for the diffusive air flow test
R	the universal gas constant, 82.06 ($mL.atm.mol^{-1}.K^{-1}$)
T	absolute temperature (K)
TMP	transmembrane pressure (kPa)
V	the hold-up volume or pressurized volume (L)
V_{filt}	filtrate pipework volume (L)
V_{O2}	molar volume of oxygen (cm^3/g)

W	weight of polymer per mL in latex (g)
y'_r	mole fraction of each component of air
β	ratio of saturation concentration of air in natural water to the saturation concentration of air in pure water
γ	surface tension of the wetting liquid in ($N.m^{-1}$)
θ	contact angle between the liquid and the membrane (degrees)
ϵ	void fraction of the membrane (membrane porosity)
ζ	pore tortuosity
κ	the membrane parameter (m^{-1})
ρ	density of water ($kg.m^{-3}$)
ρ_p	density of polymeric beads (typically 1.05 g/mL)
μ_{air}	viscosity of air (centipoises)
μ_{water}	viscosity of water (centipoises)
ψ_{H2O}	association parameter

CHAPTER 1. GENERAL INTRODUCTION

1.1 BACKGROUND

Outbreaks of waterborne diseases in the past decade in North America have raised public concerns regarding the safety of drinking water supplies. In response to these outbreaks, regulatory agencies have introduced increasingly stringent water quality regulations particularly with regard to microbial quality of drinking water. At the same time, low-pressure membranes have enjoyed exceptional growth in the water treatment field. Two factors contributed to such rapid growth; a continual drop in membrane manufacturing costs and high efficiency of low-pressure membranes in removing many microbial pathogens of interest to the water industry. Intact microfiltration (MF) and ultrafiltration (UF) membranes have been proven to be absolute barriers against protozoa such as *Cryptosporidium* spp. and *Giardia* spp., as well as bacteria pathogens (Jacangelo et al. 1991a; Jacangelo et al. 1991b; Adham and Jacangelo 1994; Freeman et al. 1996; Chow et al. 1997; Hirata and Hashimoto 1998; Karimi et al. 2002). In addition to excellent microbial removal efficiency, MF and UF membranes have other advantages over conventional water treatment processes including consistently superior finished water quality, less chemical use, considerably smaller footprints, ease of expansion, and potential for lower operating and maintenance costs. For these reasons, MF and UF membranes are now considered by many utilities as the technology of choice for new water treatment plants, as well as for upgrade of existing facilities. In 2001, over 120 membrane water treatment plants were in operation or under construction in the United States (USEPA 2001a) and this number has increased considerably since. According to the USEPA (2001), the projected production capacity in 2001 was 920 MLD (243 MGD) compared with just 26.5 MLD (7 MGD) in 1996. The treatment capacity of membrane plants has also increased in recent years from an average of 10 MLD to over 260 MLD in the past couple of years. For example, the City of Minneapolis, Minnesota is planning a 260 MLD (70 MGD) facility for startup in 2004 (USEPA 2001a). Here in Canada, the City of Kamloops in British Columbia has selected an immersed membrane water treatment plant with chemical pretreatment, having a capacity of 160 MLD (42 MGD) for commissioning in 2005 (Zenon Environmental 2002).

There are, however, at least two outstanding issues with respect to microbial removal efficacy of low-pressure membranes. First, although intact MF and UF membranes have shown to be effective barriers against many pathogenic microorganisms, the same cannot be said about membranes that lack integrity. Microbial removal of MF and UF membranes may be hampered by the lack of membrane integrity. Breach of membrane integrity may occur in the event of fibre breakage, presence of oversized pores, manufacturing defects, and seal malfunction. There are several tests that can be employed to monitor the integrity of low-pressure membranes. Collectively, these tests are referred to as membrane integrity monitoring tests. Most regulatory agencies in North America and Europe currently require membrane water treatment facilities to conduct regular integrity monitoring tests to ensure that they meet the removal credits assigned to their respective membrane facilities (Van Genderen and Hegarty 1998; Allgeier 2001; Hall et al. 2003). A detailed review of integrity monitoring test for low-pressure membranes is presented in Chapter 2 of this thesis. Although several membrane integrity tests are currently being used by the membrane water treatment industry, there are a number of outstanding issues with respects to these tests that must be addressed. These issues include improving the sensitivity of integrity monitoring tests, identifying the impact of operating conditions such as water temperature and fouling on integrity test results and developing a meaningful relationship between the test results and microbial removal efficiency of low-pressure membranes. These issues are further explored in subsequent sections of this chapter. The first portion of this thesis is an attempt to address the outstanding issues with respect to membrane integrity monitoring tests.

The second issue with respect to microbial removal efficacy of low-pressure membranes is their ability to remove viruses. Unlike UF membranes which have shown a more consistent removal pattern for viruses, MF membranes have been very inconsistent in removing viruses. Several researchers have investigated the mechanism of virus removal by MF and UF membranes (Urase et al. 1993; Urase et al. 1994; Jacangelo et al. 1995; Madaeni et al. 1995; Herath et al. 1998; Herath et al. 1999). In general, most UF membranes seem to provide near complete rejection of viruses. Microfiltration membranes on the other hand, show inconsistent removal patterns that range from zero to over 3 logs of viruses removed. Both Madaeni et al. (1995) and Herath et al. (1999) for example, have shown that relatively high removal of viruses may be achieved under appropriate conditions. In one case, these appropriate conditions included crossflow, low transmembrane pressure, and presence of biomass and turbidity (Madaeni et al. 1995). In another case, low pH (near the isoelectric point of the specific virus) was most conducive to virus rejection (Herath et al. 1999). It is therefore important to establish the most appropriate conditions for the removal of viruses by MF membranes. This would be useful not only to membrane water treatment utilities for improved virus rejection, but also to regulatory bodies responsible for establishing log removal credits for MF facilities. The second portion of this thesis is dedicated to establishing the optimum conditions for virus removal, using MF membranes.

It is the opinion of the author that addressing deficiencies associated with the present membrane integrity monitoring tests, as well as identifying optimum conditions for virus removal with MF membranes, will advance the science of membrane filtrations and greatly enhance its application for water and wastewater treatment.

1.2 OVERVIEW OF LOW-PRESSURE MEMBRANE PROCESSES

Membranes are semi-permeable barriers that allow passage of certain materials while retaining others. The driving force for separation in membrane processes can be pressure differential, concentration gradient, partial pressure, temperature, or electrical potential. For most membranes utilized in water treatment industry, the driving force is pressure differential, commonly referred to as transmembrane pressure (TMP). Low-pressure membranes are typically divided into two main categories; microfiltration (MF) and ultrafiltration (UF). They are called low-pressure since they operate at much lower pressures than nanofiltration or reverse osmosis membranes. Typical TMP for MF and UF membrane ranges from 20 to 275 kPa (3 to

40 psi), with UF membranes operating at the upper end of this pressure range. There are also low-pressure membranes that operate under a suction pressure (vacuum) ranging from -20 to -80 kPa (-3 to -12 psi) (USEPA 2001a). Rejection characteristics of MF and UF membranes are usually specified in terms of either pore size (in case of MF membranes) or molecular weight cut-off (MWCO, in case of UF membranes), although, at times, UF membranes are also characterized by their pore size. Membrane manufacturers use two different ways to specify membrane pore size, the nominal pore size or the absolute pore size. The nominal pore size is defined based on a certain percentage removal (typically 90%) of particulate matter of a certain size. The absolute pore size is usually the largest pore size of a membrane and is determined based on 100% removal of particulate matter of a certain size. MF membranes used for water treatment typically have pores sizes ranging from 0.1 to 0.2 μm. The MWCO designation for UF membranes refers to the molecular weight of solute that is 90% rejected by the membrane (Cheryan 1998). The MWCO for UF membranes used for water treatment is typically greater than 100,000 to 500,000 Dalton (USEPA 2001a). The absolute pore size for most UF water treatment membranes ranges from 0.01μm to 0.05 μm.

Polymeric MF and UF membranes, which are used predominantly in water treatment, are manufactured from a variety of polymers including polypropylene, Polyvinylidene fluoride (PVDF), polysulfone, polyethersulfone and cellulose acetate. Rejection and flow characteristics of a membrane can be strongly affected by the type of polymer and membrane surface modifications. Of the four main types of pressure-driven membrane systems, spiral wound, plate-and-frame, tubular, and hollow fibre, the hollow fibre modules are the most prevalent among low-pressure water treatment membranes. Plate 1.1 shows a typical submerged-type hollow-fibre membrane module. Hollow fibres have a very small inside diameter, typically less than 1.2 mm. The wall thickness varies from system to system but typically is in fractions of millimeters. Plate 1.2 shows a Scanning Electron Microscopy (SEM) image of the cross-section of a hollow fibre membrane.

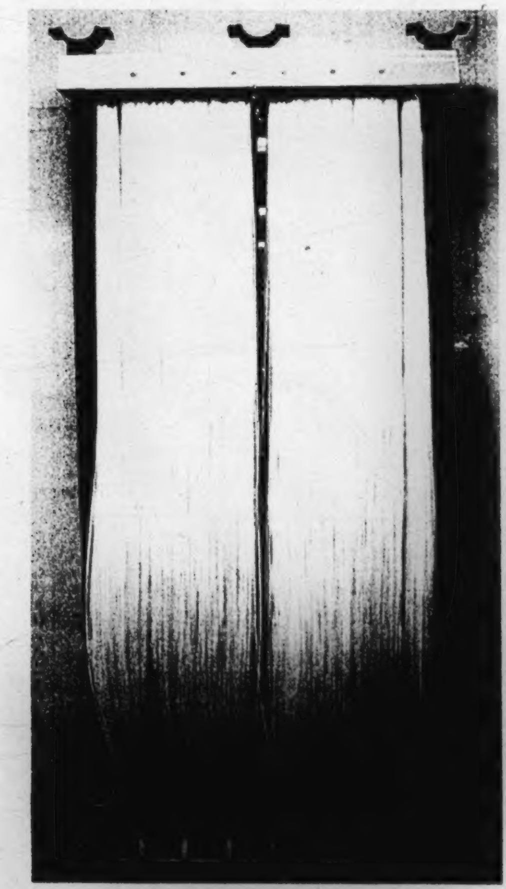

Plate 1.1 A submerged-type hollow fibre membrane module.

Most low-pressure hollow-fibre membranes are operated in a crossflow, dead-end modes or a combination thereof. Under crossflow conditions, the membrane feed passes tangentially over the membrane surface to generate high shear and minimize fouling. In a dead-end mode, the feed flows perpendicular to the membrane surface (much like conventional sand filtration). Most membrane manufacturers operate in dead-end mode when treating low-turbidity waters, since energy consumption is less in this mode. Under the dead-end mode of operation, all of the feed, with the exception of what is wasted for backwash, is converted to finished water (permeate). The crossflow mode of operation typically generates a third stream referred to as the reject or concentrate.

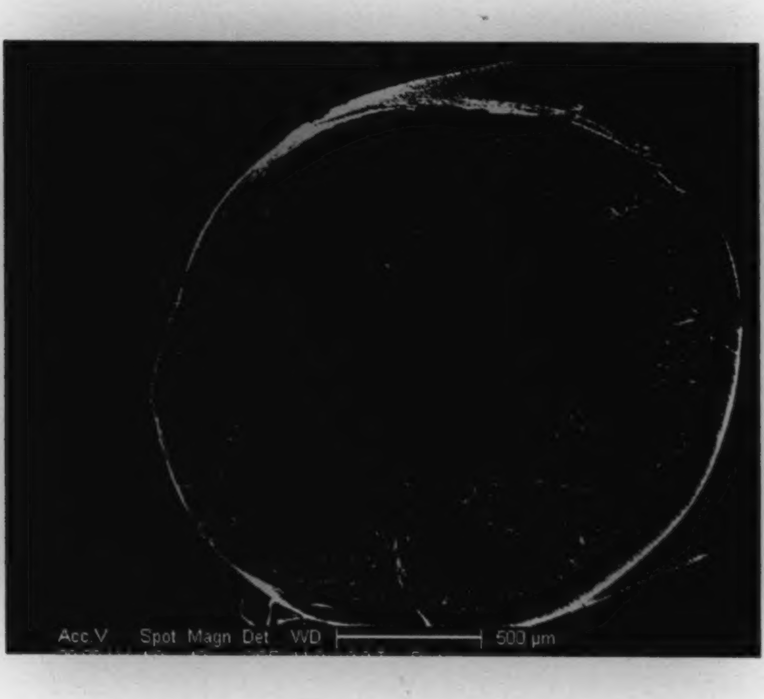

Plate 1.2 SEM image of a hollow fibre membrane

Similar to conventional filtration, membrane production is expressed as the permeate flux in units of volume per time per surface area (e.g. L.m^{-2}.h^{-1}). A more useful presentation of membrane performance is specific flux (J_{sp}) which is the ratio of permeate flux (J) to TMP (P_{TMP}) as shown in Equation 1.

$$J_{sp} = \frac{Q}{A \bullet P_{TMP}} \qquad [1]$$

where Q is the permeate flow (L/h) and A is the membrane's surface area (m^2). The permeate flux and consequently the specific flux are functions of temperature and, in most cases, these values are corrected to 20°C using temperature relationships for water viscosity. Several relationships are available to express change of water viscosity with water. Karimi et al (1999) provided the following relationships for a microfiltration system.

$$\text{(For T} \leq 20\,^{\circ}\text{C)} \quad \mu_T = e^{-0.0282(T-20)} \qquad [2]$$

$$\text{(For T} > 20\,^{\circ}\text{C)} \quad \mu_T = e^{-0.021(T-20)} \qquad [3]$$

Where, μ_T is the viscosity of water at temperature T.

All membranes suffer in varying degree from fouling. Membrane fouling occurs when solute or particulate matter accumulates on the surface (cake layer formation) or pores (pore plugging) of the membrane and result in decreased membrane performance (lower flux, higher TMP). Fouling is ultimately irreversible, requiring chemical cleaning to restore membrane performance. However, the short-term impact of fouling may be reduced by backpulsing or backwashing of the membrane. Backpulsing is the process of partially removing the fouling layer by either reversal of the flow or by injecting high pressure air. All low-pressure membranes require periodic backpulsing lasting from few seconds to a couple of minutes. During backpulsing, some of the permeate or feed is used to wash the foulants, producing a certain volume of backwash wastewater that must be treated and disposed of.

1.3 REGULATORY PERSPECTIVE

Since the demand for low-pressure membranes in water treatment industry continues to grow, additional membrane-specific regulations are beginning to emerge. The Guidelines for Canadian Drinking Water Quality (Health Canada 2001) does not refer to a specific technology and set guidelines for water quality only. Most provincial guidelines do not specifically regulate membrane filtration and generally tend to follow regulatory trends in the United States with respect to drinking water quality. This section therefore, focuses primarily on the current and upcoming regulations in the US. When the Surface Water Treatment Rule (SWTR) was promulgated in 1989, low pressure membranes were still an emerging technology and few, if any, such installations existed in North America. Consequently, the SWTR did not refer to low-pressure membranes and was primarily concerned with conventional water treatment technologies such as granular media filtration (USEPA 1991). The SWRT assigned conventional sand filtration log removal credits of up to 2.5 and 2 logs for *Giardia* spp. and viruses, respectively. The Interim Enhanced SWTR (IESWTR) introduced *Cryptosporidium* spp. removal credits of up to 2.5 logs for conventional filtration. The IESWTR also lowered the maximum allowable filtered water effluent turbidity to 0.3 NTU from 1 NTU and required all facilities treating surface water (or groundwater under the influence of surface water) for greater than 10,000 people to conduct continuous turbidity monitoring of their filtered water (USEPA 1998). The intent of such requirements was to ensure that a certain degree of *Cryptosporidium* spp. removal is achieved in the treatment process. The Long Term 1 ESWTR (LT1ESWTR) extended the requirements of the IESWTR to communities with less than 10,000 people. Neither the IESWTR nor the LT1ESWTR provide regulations governing the use of low-pressure membranes and defining the associated log removal credits. However, different states have been regulating membrane filtration plants based on the provisions for the "alternative filtration technologies" (AFT) in the IESWTR. These states, based on the results of verification studies and other pilot studies, have developed log removal credits for MF and UF membranes for *Cryptosporidium* spp. and viruses. Assigned removal credits for *Giardia* spp. and *Cryptosporidium* spp. vary from state to state and range from 1 to 4 logs for *Giardia* spp. (12 states) and 2 to 4 logs (only two states) for *Cryptosporidium* spp. Virus removal credits vary from zero to 0.5 (two states) logs for MF plants and 4 logs for UF plants (two states) (USEPA 2001a).

The proposed Long Term 2 ESWTR (LT2ESWTR), however, places a major emphasis on alternative treatment technologies, including UF and MF membranes.

The proposed LT2ESWTR defines membrane filtration as "a pressure or vacuum-driven process in which particulate matter larger than 1 μm is rejected by an engineered barrier, primarily through a size exclusion mechanism, and which has a measurable removal efficiency of a target organism that can be verified through the application of a direct integrity test" (USEPA 2001b). The LT2ESWTR proposes a "bin" system to categorize all surface water treatment facilities with respect to additional *Cryptosporidium* spp. removal requirements beyond the required 2.5 log for granular media filtration. A total of four "bins" have been proposed with additional *Cryptosporidium* spp. removal requirements ranging from zero for utilities with less than 0.075 *Cryptosporidium* spp. per liter of their source water to an additional 2.5 log removal for systems with greater than 3.0 *Cryptosporidium* spp. per litre of source water. Additionally, the LT2ESWTR proposes a "microbial toolbox" which the utilities can use to select technologies for addressing the additional *Cryptosporidium* spp. removal requirements.

According to the proposed LT2ESWTR, a membrane process can receive *Cryptosporidium* spp. removal credits by either demonstrating its removal efficiency through challenges testing or by determining a maximum log removal value based on the results of a direct integrity monitoring test. The proposed rule provides brief guidelines for conducting challenge testing and sets performance criteria for direct integrity monitoring tests.

In terms of challenge testing, the rule allows the use of either *Cryptosporidium* spp. oocysts or an appropriate surrogate which can be shown to be removed more efficiently than *Cryptosporidium* spp. oocysts. The challenge testing can be performed on a full-scale or a smaller scale module, if challenge results and integrity test results are scaleable to full-scale performance.

The direct integrity tests provide instantaneous information on breach of membrane integrity or microbial removal efficacy of a membrane system. These tests can be classified into two main categories: pressure-driven tests and marker-based tests. The pressure-driven integrity tests, such as pressure decay test (PDT) and diffusive air flow tests (DAF) rely on the measurement of pressure drop or air flow rate across an intact wetted membrane. Marker-based tests measure the removal of inert particles in specific size ranges or molecular markers by the membrane and thereby establish log removal values (LRV) for the particular marker. The proposed LT2ESWTR establishes three criteria for direct membrane integrity tests; resolution, sensitivity, and frequency. Resolution has been defined as the ability of the direct integrity test to detect breaches of membrane integrity in the order of 3μm or less (within the size range of *Cryptosporidium* spp.). The sensitivity criterion, on the other hand, requires that the integrity test be able to verify, as a minimum, the log removal credits that have been awarded to the membrane system. The proposed rule defines sensitivity, in terms of verifiable log removal, by Equation 4:

$$LR_{Max} = LOG\left[\frac{Q_{Filtrate}}{CF \times Q_{Breach}}\right] \qquad [4]$$

where LR_{Max} is the maximum log removal value that can be verified by a direct integrity test, $Q_{Filtrate}$ is the total design permeate flow from the membrane unit, Q_{Breach} is the total flow from the smallest breach that the direct integrity test can detect, and CF is the concentration factor. Concentration factor must be defined by each membrane manufacturer and is a measure of increase in the concentration of contaminants in contact with the membrane relative to the feed water. The actual magnitude of the CF may vary from 1 to 20, for different membrane systems.

Currently, the LT2SWTR proposes that periodic direct integrity tests be conducted on each membrane module at least once every 24 hours during the operation of the unit. The choice of the type of direct integrity test depends on the preference of the manufacturer and the utility, as long as the test meets the requirements of the LT2ESWTR. There are also indirect integrity tests which provide indirect indication of the breach of membrane integrity, based on monitoring a surrogate in the permeate such as turbidity or particle count. The LT2ESWTR proposes continuous indirect integrity tests for all membrane plants in form of turbidity monitoring. According to the proposed rule, continuous turbidity monitoring of the permeate should be conducted on each unit with turbidity values not exceeding 0.1 NTU. Breach of membrane integrity should be signalled if two consecutive turbidity readings exceed 0.15 NTU.

The proposed LT2ESWTR has prompted the USEPA to begin preparing a guidance manual for membrane filtration to assist utilities and manufacturers in meeting the proposed rule. This guidance manual would be a great step in developing a standard approach in determining the microbial removal efficiency of membrane water treatment plants and would provide standard procedures for conducting direct integrity monitoring, as well as challenge tests.

1.4 IMPROVING MEMBRANE INTEGRITY MONITORING TESTS

The American Water Works Association Research Foundation (AWWARF) established five criteria for an ideal integrity monitoring technique (AWWARF 2000). These criteria included continuity, sensitivity, reliability, identifiability, and economy. According to AWWARF, an ideal membrane integrity monitoring test should be performed on-line and in a continuous fashion, must be able to detect small breaches in membrane integrity under full-scale operations, should not produce false negative or false positive signals, should be able to identify the individual compromised fibres, and must be economically feasible. The three criteria of resolution, sensitivity and frequency proposed in the LT2ESWTR seem to encompass most of the AWWARF requirements, while placing the main emphasis on determining microbial removal efficiency of membranes. In other words, the proposed LT2ESWTR appears to put the membrane integrity monitoring tests into a clear perspective. The ultimate criteria therefore seems to be the ability of a direct integrity test to reliably, consistently, and safely determine removal values achieved by a membrane unit at least once every 24 hours of operation. Currently, the emphasis is on the removal of *Cryptosporidium* spp. and hence a direct integrity test should reliably detect breaches of membrane integrity less than 3 μm in size.

As mentioned earlier, there are two main categories of membrane integrity tests; direct integrity tests and indirect integrity tests. The direct tests are divided into two categories as well; pressure-based tests and marker-based tests. The pressure-based tests are conducted with the membranes offline and use air pressure to detect the presence of a hole or defect. The most widely used pressure-based direct integrity test is the pressure decay or pressure hold test. This test measures the loss of pressure that results from diffusion of air through an intact membrane and passage of air through a defect. Necessary equipment for a pressure decay test is supplied by almost all membrane manufacturers as standard equipment and the test is programmed to run automatically on preset intervals. Another pressure-based test is the diffusive air flow test that measures the volume of air that diffuses through membrane pores or flows freely through defects. Presently, only one manufacturer uses this test and the test equipment is not part of standard supply. A third pressure-based test is called vacuum decay test and has been part of integrity testing in the reverse osmosis industry for some times. At least one membrane manufacturer is attempting to develop a vacuum hold test for low-pressure membranes.

Marker-based tests propose to use molecular markers or latex microspheres (latex beads) or other particles for determining the integrity of membrane units. These tests are similar to a challenge test in that they challenge a membrane with specific particles and measure log removal of particles. Aside from the spiked integrity monitoring (SIM) that uses activated carbon particles of certain size range, other marker-based tests are still under development. Currently, one membrane manufacturer uses SIM in a few of its installations.

A third category of tests, referred to as diagnostic tests, include such tests as the bubble point test and the acoustic test. The acoustic test is based on the detection of the noise generated by passage of water at high pressure through a hole or defect. It is used to identify compromised modules, once the lack of membrane integrity of a system has been determined by direct integrity tests. The bubble point test is used to identify compromised fibres and is based on the visual detection of air bubbles leaving a pressurized compromised fibre that is immersed in water.

The indirect integrity monitoring tests rely on monitoring a surrogate such as turbidity or particle count in the permeate. It is difficult to relate these tests to microbial removal and, as such, these tests cannot be used as a stand-alone-test for monitoring membrane integrity. Membrane utilities however, are required to conduct continuous turbidity monitoring or particle counts to meet regulatory requirements. These tests cannot detect small breaches of membrane integrity (lack required resolution) but have been used to detect gross breaches in the integrity of a membrane system.

This thesis is primarily concerned with the pressure-based direct integrity monitoring tests.

1.4.1 Improving the Resolution and Sensitivity of the Direct Integrity Tests

Using the three criteria of resolution, sensitivity and frequency proposed in the LT2ESWTR, one can evaluate the current pressure-based direct integrity tests and identify their deficiencies. The pressure decay test would be the focus of this evaluation, since it is by far the most widely used direct integrity test for low pressure membranes.

Resolution of most direct integrity monitoring tests (i.e. the smallest defect that can be detected) is partly a function of the test starting pressure. The size of the largest defect that can be detected by a pressure-based integrity test can be estimated by Equation 5 (Schroeder and Deluca 1980):

$$P = \frac{4k\gamma\cos\theta}{d} \qquad [5]$$

where P is the *test* pressure (Pa), k is the correction factor for the shape of the largest pore, γ is the surface tension of the wetting liquid in (N/m), θ is the contact angle between the liquid and the membrane, and d is the diameter of the largest pore (m). Assuming a perfectly round pore (i.e. k=1) and contact angle of zero degrees, a test pressure of about 97 kPa (14 psi) is required to detect a 3 μm defect as required by the LT2ESWTR. Most low-pressure membranes are capable of conducting pressure decay tests at such a pressure and therefore seem to have sufficient resolution to meet the LT2ESWTR requirement. Although it is possible to register a response with a 3 μm or smaller defect in a small system, background noise generated from air diffusion in a membrane with large surface area will most likely mask the response from a pressure decay test. This phenomenon, sometimes referred to as the dilution effect, has been observed before. In a full-scale study, (Landsness 2001) showed that pressure decay test results were only significant after 6 out of 1.8 million fibres were cut. The results of pressure decay tests for less than six broken fibres were within the normal variation of a unit with no compromised fibres. Therefore, the contribution of diffusion of air through intact pores of a membrane unit should be estimated and accounted for in interpreting the response of a pressure decay test. Such a contribution, if closely estimated, can provide a baseline value for a specific system against which the pressure decay test results can be evaluated.

The criterion of sensitivity proposed by the LT2ESWTR requires that the direct integrity test be able to verify, as a minimum, the log removal values assigned to a membrane system. Most membrane manufacturers have developed theoretical relationships to relate the results of a direct integrity test to microbial removal. US Filter/Memcore, for example, uses the following relationships (see Equations 6 and 7) for the pressure decay and diffusive air flow tests (Johnson 1998; Hong et al. 1999).

$$LRV = \log\left[\frac{Q_{filt} P_{atm}}{V_{filt}} \frac{\mu_{water}(P_{test}^2 - P_{atm}^2)}{2\mu_{air} P_{filt} P_{atm}} \left(\frac{t}{\Delta P}\right)\right] \qquad [6]$$

$$LRV = \log\left[\frac{Q_{filt}}{Q_{DAF}} \frac{\mu_{water}(P_{test}^2 - P_{atm}^2)}{2\mu_{air} P_{filt} P_{atm}}\right] \qquad [7]$$

where, LRV is the log removal values that a membrane can achieve, Q_{filt} is filtrate flow rate (L/min), Q_{DAF} is air flow rate from a DAF test result (L/h), μ_{water}, μ_{air} are viscosity of water and air respectively (kg/m.s), P_{test}, P_{filt}, and P_{atm} are test air pressure, transmembrane pressure and atmospheric pressure (kPa), respectively, V_{filt} is filtrate pipework volume and $\Delta P/t$ is pressure decay rate (kPa/min). According to the above relationships, higher pressure decays or diffusive air flow rates result in lower estimated LRV. In a recent study Trimboli (2001) showed that Equations 6 and 7 consistently underestimated actual log removals achieved by a full-scale microfiltration plant challenged with spores of *Bacillus megaterium*. The above relationships can estimate higher and more representative LRV if the contribution of air diffusion through intact pores is accounted for in determining the pressure decay or diffusive air flow rates. In another recent challenge study using spores of *Bacillus subtilis*, Côté (2003) found that theoretical LRV relationships underestimated actual LRV by as much as 2.5 logs. However, accounting for the contribution of diffusion, as shown in Equation 8, resulted in more representative estimates of LRV.

$$PDR_{corrected} = PDR_{measured} - PDR_{diffusion} \qquad [8]$$

where, $PDR_{diffusion}$ is the pressure decay rate observed for an intact system due to diffusion.

Consequently, estimating and accounting for the contribution of diffusion will greatly improve the sensitivity of pressure decay tests.

1.4.2 Impact of Operating Conditions on Pressure-Based Integrity Tests

As discussed earlier, diffusion of air through intact pores of a membrane may have a considerable impact on the pressure-based direct integrity tests. It is therefore important to identify factors which may impact the diffusion process and hence impact the results of a pressure-based integrity test. While evaluating the integrity of small flat-sheet microfiltration membranes, (Hofman 1984) suggested the following relationship (based on the Fick's first law of diffusion) for estimating the contribution of diffusion during a pressure decay or diffusive air flow test.

$$N = \frac{DH(P_1 - P_0)}{L} \varepsilon A \qquad [9]$$

where, N is the molar flow rate of diffused air, mol.s^{-1}, D is the diffusivity constant for air-water system, m^2.s^{-1}, H is Henry's Law constant for the gas used, air in this case (mol.atm^{-1}.m^{-3}), P_1 and P_0 are test and the downstream pressures, respectively (atm), ϵ is the void fraction of the membrane (membrane porosity), A is membrane's surface area, (m^2), and L is the length of the diffusive path which is equal to the wall thickness for a hydrophilic membrane with cylindrical pores, (m).

Therefore, factors that can affect diffusivity, such as Henry's constant, membrane porosity, downstream pressure, and length of diffusive path may also affect the rate of air diffusion and hence impact the pressure decay or diffusive air flow test results. One such factor is water temperature. Water temperature affects its' viscosity, density, surface tension, contact angle and the membrane material, all of which can impact the diffusion of air through a column of water. The effect of temperature on the rate of diffusion of nitrogen through an intact flat sheet membrane was observed by (Hofman 1984). He found that an increase in water temperature resulted in an increase in rate of diffusion of nitrogen up to 60°C, above which increasing temperature decreased the rate of diffusion. Determining the impact of temperature on a pressure decay test therefore is important, especially for locations with significant seasonal variations in raw water temperatures such as Canada. Another factor that may affect diffusion is membrane fouling. Fouling resulting from cake layer formation or pore plugging can reduce membrane porosity markedly, which, in turn would reduce the rate of diffusion (see Equation 9). The impact of fouling on the rate of air diffusion through an intact membrane has not been studied in detail before this work. And finally, pressure decay tests for immersed membranes are conducted with the membrane fully submerged. Submergence of membrane contributes to the downstream pressure (P_0 in Equation 9) and can consequently impact the rate of diffusion.

1.5 VIRUS REMOVAL WITH MICROFILTRATION MEMBRANES

Aside from the membrane integrity monitoring, inconsistent virus removal by MF membranes has been another outstanding issue with respect to microbial removal efficacy of low-pressure membranes. As discussed earlier, only two U.S. states award MF membranes log removal credits for viruses; a meager 0.5 log, while several states award UF membrane virus log removal of up to 4 logs. The hesitancy of regulatory agencies to award MF membranes high virus removal credits is well founded. Viruses have shown inconsistent virus removal ranging from zero to over 3 logs. As pore sizes of most MF membranes is higher than 0.1 μm, larger than the size of largest virus, most viruses are expected to pass through a MF membrane unhindered. Several factors, however, seem to play important roles on the ability of MF membranes to reject viruses. As virus removal by MF membranes may take place by adsorption of virus on the membrane's surface or pores, factors that enhance virus adsorption such as pH and conductivity (Urase et al. 1993; Herath et al. 1999) may impact virus rejection by MF membrane. Other factors that can alter water chemistry or impact the electrostatic interactions between viruses and membrane materials can also influence the rate of virus removal by MF membranes. Prominent among such processes is chemical coagulation, which can influence virus removal not only by altering the surface charge of viruses but also by agglomerating viruses into larger particles that MF membranes can reject by mere straining. Membrane fouling, on the other hand, may also impact virus removal (Jacangelo et al. 1995) as fouling causes additional resistance against passage of particulate matter. Other factors such as permeate flux or initial numbers of viruses in the feed, as well as the presence of other particulate matter in raw water, may also impact the ability of MF membranes for virus removal.

Although some researchers have investigated the impact of pH and conductivity on the removal of viruses by MF membranes (Urase et al. 1993; Herath et al. 1999), no study has investigated the impact of interaction between conductivity and pH on virus rejection. Neither has the impact of coagulation on virus removal by MF membranes been evaluated in detail. The relationship between adsorption and fouling as two mechanisms responsible for virus rejection by MF membranes has also not been adequately investigated. It is important to develop a better understanding of the impact of the above factors in order to enhance the ability of MF membranes for virus removal. It is also important from the regulatory point of view to utilize such understanding in assigning credits for virus removal to MF membranes under different water treatment conditions. In addition, with increasing incorporation of MF membranes into existing conventional water treatment facilities or new facilities with chemical pretreatment, the role of coagulation on virus rejection by MF membrane must be better delineated.

1.6 OBJECTIVES AND SCOPES OF THE RESEARCH PROGRAM

As mentioned earlier, there are at least two outstanding issues associated with the microbial removal efficacy of low-pressure membranes. The first issue relates to membrane integrity monitoring tests and developing a reliable test that can, on a frequent basis, provide real-time information on the effectiveness of UF and MF membranes to remove microbial pathogens of interest (*Cryptosporidium* spp. in the case of the proposed LT2ESWTR). The second issue deals with the inconsistent virus removal by MF membranes and determination of conditions under which MF rejection of viruses is optimal. Therefore, this research program was designed to address two main objectives:

(1) Improving the resolution and sensitivity of current pressure-based integrity monitoring tests for low-pressure membranes; and

(2) Improving the efficacy of MF membranes in removing viruses.

Within the context of the above objectives, this research program aimed at improving the understanding of the fundamentals of pressure-based membranes, addressing their most outstanding deficiencies, and providing practical tools for membrane manufacturers and utilities to ensure their compliance with the current and forthcoming regulations. In addition, a systematic approach was undertaken to improve the knowledge of the fundamental processes involved in and determination of optimum conditions for virus removal by MF membranes. Achieving the above objectives within the confines of this research project involved several strategies as summarized below.

(1) Development of an extensive knowledge base with respect to both theoretical and practical consideration associated with current integrity monitoring tests for low-pressure membranes (Chapter 2);

(2) Addressing the resolution and sensitivity issues associated with pressure-based direct integrity monitoring tests by developing a theoretical model to estimate the contribution of diffusion to pressure decay and diffusive air flow tests (Chapter 3);

(3) Further improvement of the diffusion model by determining the impact of variables such as water temperature, membrane fouling and submergence on air diffusion through an intact membrane (Chapter 4);

(4) Verifying the diffusion model under pilot-scale conditions and evaluating its effectiveness in providing reliable verification of log removal values by conducting challenge studies (Chapter 5);

(5) Developing a reliable marker-based integrity monitoring test by evaluating the viability of fluorescent latex microspheres (latex beads) as surrogates for *Cryptosporidium* spp. (Chapter 6);

(6) Investigating the mechanisms for virus removal by MF membranes using bacteriophages native to secondary effluent (Chapter 7);

(7) Evaluating the interaction between pH and conductivity and investigating the impact of coagulation on the rejection of viruses by MF membranes (Chapter 8);

(8) Identifying issues associated with chemical pretreatment prior to membrane filtration (Chapter 9); and

(9) Evaluating the benefits of chemical pretreatment such as coagulation on the performance of low-pressure membranes (Chapter 10).

As the result of this research program, a model was developed that, based on Fick's first law of diffusion, provides an accurate estimate of the contribution of air diffusion to pressure decay for an immersed membrane. Another model was developed to describe the impact of water temperature on diffusive air flows and pressure decay tests. It was shown that membrane fouling has a noticeable impact on the rate of diffusion through an intact membrane and attempts were made to qualitatively explain the impact of submergence on the rate of diffusion.

A better understanding of the mechanisms involved in rejecting viruses was gained and the effect of pH on the inactivation of MS2 phage and its removal by MF membranes was clarified. It was shown that chemical coagulation can improve the rejection of viruses by MF membranes. It was also shown that aside from improving the rejection of viruses, chemical coagulation markedly improves the performance of low-pressure membranes by retarding the rate of membrane fouling. Finally, an extensive review of the impact of chemical pretreatment on low-pressure membranes was undertaken and several outstanding issues were identified for future research.

In conclusion, this research project has made several unique contributions to the understanding of the fundamental processes associated with low-pressure membrane filtration that should help improve MF and UF processes for water and wastewater treatment. Practical implications of this work would assist regulatory bodies as well as membrane manufacturers and utilities in monitoring the microbial removal efficacy of low-pressure membranes. Most importantly, as every fundamental work must have tangible public benefits, the author believes that the outcome of this project will enhance the ability of membrane water treatment utilities to ensure the protection of public health.

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CHAPTER 2. MONITORING THE INTEGRITY OF LOW-PRESSURE MEMBRANES – A REVIEW[*]

2.1 INTRODUCTION

The search for alternative water treatment technologies has gained new momentum with the promulgation of the United States Surface Water Treatment Rule (SWTR) and the implementation of the Interim Enhanced SWTR (IESWTR). One of the goals of the IESWTR is to improve the removal of microbial pathogens, specifically *Cryptosporidium* spp., while minimizing the formation of disinfection byproducts (USEPA 1998). In addition, the proposed Long Term 2 ESWTR includes source water quality-based requirements for up to 2.5-log inactivation or removal of *Cryptosporidium* spp. beyond conventional treatment. The efficacy of low-pressure membranes in removing total coliform (TC) bacteria, *Giardia* spp. and *Cryptosporidium* spp. has been demonstrated by several researchers (Jacangelo et al. 1991a; Jacangelo et al. 1991b; Adham and Jacangelo 1994; Adham et al. 1996; Freeman et al. 1996; Hirata and Hashimoto 1998). However, the effectiveness of microfiltration (MF) and ultrafiltration (UF) in removing microbial pathogens can be hampered by the lack of membrane integrity. Monitoring the integrity of UF and MF membranes therefore, is of utmost importance in producing treated water that is safe for public consumption. Increasing numbers of regulatory agencies are also recognizing the importance of conducting regular integrity monitoring tests for water treatment membranes. Allgeier (2001) surveyed 29 states with respect to regulations governing MF and UF water treatment membrane systems. Of the 29 U.S. states surveyed, 15 states required some form of integrity monitoring, beyond typical turbidity monitoring, for all low-pressure water treatment membrane plants. Other countries are also considering regular integrity monitoring as a requirement for all water treatment membrane plants (Van Genderen and Hegarty 1998).

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[*] A version of this Chapter was published in the American Water Works Association Journal, 95(6):95-108.

2.2 BACKGROUND

Concern regarding membrane integrity was first raised in the pharmaceutical industry long before the widespread use of UF and MF in water treatment. Low-pressure membrane filters have been used for particle removal and sterilization in pharmaceutical applications as early as mid 1930's (PDA 1998). To be classified as sterilizing grade, a membrane filter must demonstrate a log reduction value (LRV) of more than seven during a bacterial challenge test (Hofman 1984). In the past several decades, the pharmaceutical industry has used several physical techniques that, in conjunction with results from bacterial challenge tests, constitute a validation of the retention capabilities of a sterilizing membrane. These techniques include the bubble point test, the pressure hold (pressure decay) test, the diffusive airflow test, and the liquid-liquid porosimetric test (Phillips and DiLeo 1996). Of the above techniques, the first three have found widespread application in monitoring the integrity of low-pressure membranes used for water treatment. These techniques are commonly referred to as direct integrity monitoring techniques, since they provide a tool for direct determination of a compromised membrane without relying on the permeate quality. Another integrity monitoring technique that has more recently been utilized is the use of acoustic sensors to determine the presence of oversized pores or defects in a membrane module. Although this test has been classified as a direct method by USEPA (2001), the proposed LT2ESWTR classifies this test as a diagnostic test rather than a direct test. Other integrity monitoring techniques rely on monitoring a surrogate parameter in the permeate. These techniques are commonly referred to as the indirect integrity monitoring techniques. Particle counting, particle monitoring and turbidity monitoring are among the most commonly employed indirect integrity monitoring techniques (Adham et al. 1995).

2.2.1 Direct integrity monitoring techniques

Direct techniques for monitoring membrane integrity provide instantaneous information regarding oversized pores or defects in a membrane system. The theoretical basis of the most commonly used direct integrity monitoring techniques can be explained based on the bubble point pressure concept. A membrane filter can be considered a porous medium with a specific pore size distribution and certain thickness. When a hydrophilic membrane is wetted, its pores will fill with water due to capillary forces. The extent to which a pore is filled (the height of column of water inside a pore) depends primarily on the pore size. The smaller the pore diameter, the higher the water column in the pore and consequently higher pressures are needed to empty the pore. Therefore, wet membrane capillaries are impermeable to bulk flow of a test gas (aside from flow caused by diffusion) until a pressure high enough to evacuate the liquid from the largest pore is reached. This pressure is commonly referred to as the bubble point pressure and is defined as the minimum pressure at which a steady stream of bubbles is observed from the downstream side of a wet membrane. The bubble point pressure is reproducible for a specific membrane with a known pore size distribution, if the integrity of membrane filter has not been compromised.

2.2.1.1 The bubble point test

The main application of the bubble point test in the field of membrane filtration is to isolate the individual compromised fibres once the lack of membrane integrity has been determined by other methods. This is performed by pressurizing the upstream of a wetted membrane to below the bubble point pressure. A steady stream of bubbles is observed from the compromised fibre(s). Plate 2.1 shows a bubble point test being performed on a membrane module.

Plate 2.1. A bubble point test conducted on a pressurized membrane. Presence of bubbles indicates compromised fibres (Source: Adham & Gramith, 2000).

The bubble point pressure can be directly related to membrane pore size by the following relationship (Schroeder and Deluca, 1980):

$$P = \frac{4k\gamma\cos\theta}{d} \qquad [1]$$

where P is the bubble point pressure (Pa), k is the correction factor for the shape of the largest pore, γ is the surface tension of the wetting liquid in (N/m), θ is the contact angle between the liquid and the membrane, and d is the diameter of the largest pore (m). A common approach for determining the bubble point pressure has been to subject the downstream of a wet membrane to increasingly higher gas pressures until a steady stream of bubbles is observed. This manual technique is, however, subject to human errors and is also affected by the membrane's surface area. A more accurate method for determining bubble point pressure that was suggested by Johnston (1981) involves measuring the air flow rate downstream of a membrane at increasingly higher applied pressures. A typical diffusion air flow curve is presented in Figure 2.1 (Farahbakhsh & Smith, 2003a). As Figure 2.1 shows, at lower applied pressures, air flow rate through the wetted membrane is linear and due mainly to diffusion. Significant deviation from linearity occurs when the bubble point pressure is reached. At this pressure, all large pores are emptied and air flows freely through these pores giving rise to much higher air flow rates. This method of determining the bubble point pressure is more reliable and minimizes human errors as well as errors associated with larger membrane surface areas. Using this method, Farahbakhsh & Smith (2003a) were able to consistently measure an identical bubble point pressure for bench-scale hollow-fibre membranes with same materials but with different surface areas.

The bubble point pressure is also affected by water temperature. Data presented by Hofman (1984) showed that a change in water temperature from 20 to 5°C resulted in a 10% drop in the diffusive air flow rate of a test gas (nitrogen). A bubble point test performed at higher or lower water temperatures may yield a different bubble point pressure, as compared with the same test performed at 20°C. Temperature affects water's surface tension, wetting ability and, as well, the solubility and rate of diffusion of air in water. Therefore, at higher water temperatures one may expect higher volumes of air to diffuse through a wetted membrane and coalesce into bubbles at the upstream side of the membrane; giving the indication that bubble point pressure is reached.

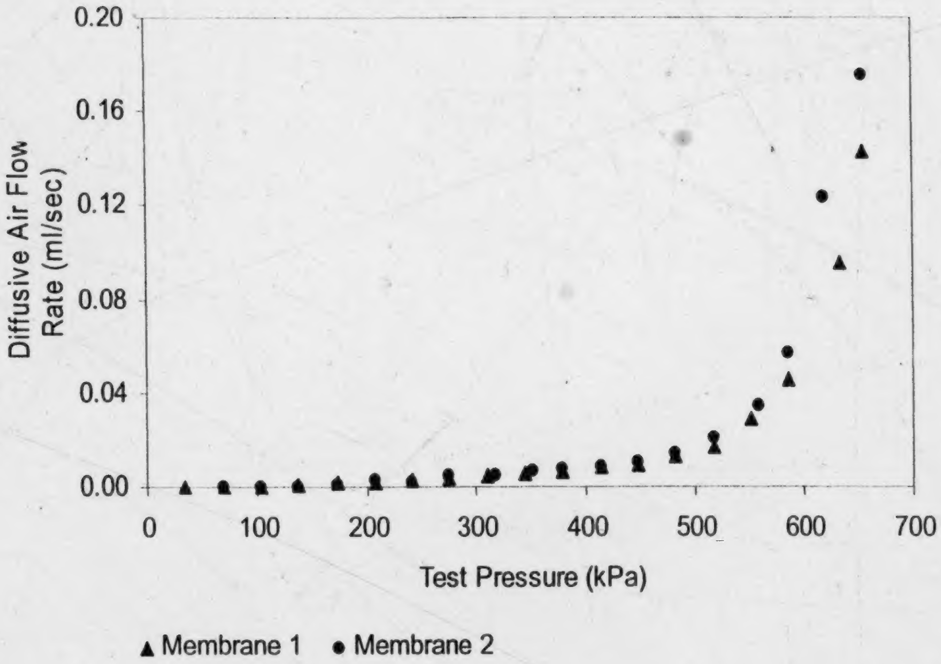

Figure 2.1 A classic diffusion air flow curve (Farahbakhsh & Smith, 2003a).

2.2.1.2 Pressure Decay and Diffusive Air Flow Tests

Both pressure decay (PD) and diffusive airflow (DAF) tests are performed while the membrane is offline. As shown in Figure 2.2, during the pressure hold or decay test, the upstream side of a wetted membrane is pressurized with air to below that of its bubble point pressure. The starting pressure for a PD or DAF tests is often substantially less than the bubble point pressure, to prevent damage to the membrane. The pressurized side of the membrane is then isolated (V1 is closed) while the shell-side is vented to the atmosphere (V2 and V3 open). The rate of pressure decay (drop) across the membrane is then monitored over a specified period of time (several minutes). In the case of a defect, a sharp drop in the pressure is observed. Figure 2.3 shows a typical result of a pass and fail pressure decay test on a membrane pilot plant with 4800 total fibres. Since the drop in the pressure may also result from system leaks, the PD test is also used to detect leaks in seals, joints and plumbing prior to commissioning a membrane system. The pressure loss caused by gas loss during a pressure decay test can be estimated by the following equation (Hofman 1984).

$$\Delta P = \frac{V_D P_{atm} T_{up}}{V_{up} T_b} \qquad [2]$$

Where ΔP is the upstream pressure loss (kPa/min), P_{atm} is the atmospheric pressure (kPa), T_b and T_{up} are the absolute downstream and upstream liquid temperatures (K), respectively, V_D is the volumetric gas loss (mL/min), and V_{up} is the volume of the filter system (the pressurized volume including the fibres and plumbing) upstream of the membrane (mL). This equation illustrates that the sensitivity of a pressure decay test is dependent on the upstream volume of the filter system. The terms T_{up} and T_b can be deleted from the above equation since, in water treatment applications, the upstream and downstream water temperatures are the same.

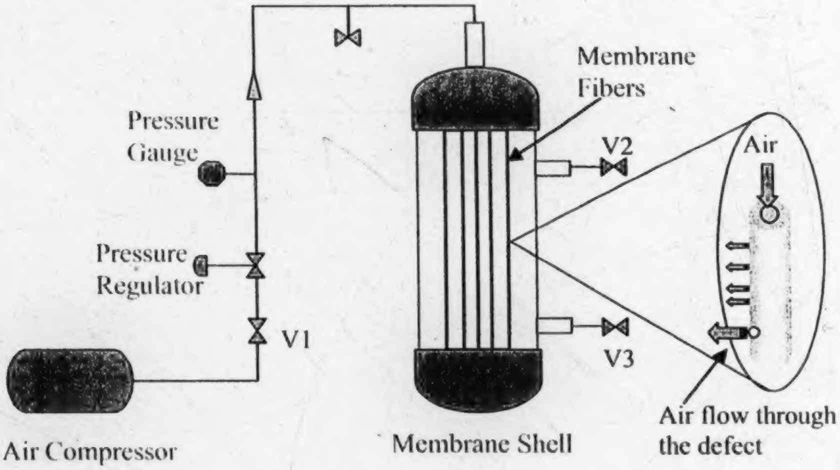
Membrane Fibers
Pressure Gauge
V2
Air
Pressure Regulator
V1
V3
Air Compressor
Membrane Shell
Air flow through the defect

Figure 2.2 . Schematic of a pressure decay test.

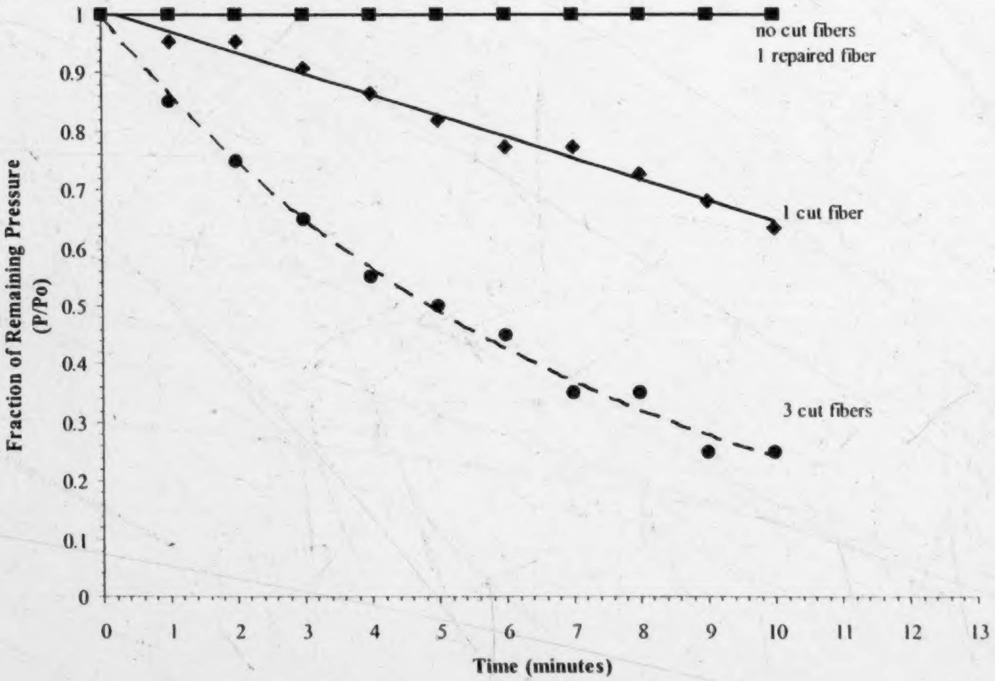

Figure 2.3 Example of an air pressure decay test for a microfilter membrane module (4800 fibres) (Source: Adham & Gramith, 1999a).

During the DAF test, the wetted membrane is pressurized with air at below the bubble point pressure in a similar fashion as shown in Figure 2.2. The shell-side is then isolated (V2 closed, V3 open to measure the volume of displaced air or liquid) and the volume of air flowing through the membrane is measured and compared with values for diffusive airflow for the intact membrane. Lack of membrane integrity is signaled if the airflow through the membrane is higher (by a predetermined amount) than the diffusive airflow through an intact membrane. Theoretical values of diffusive airflow for a membrane can be estimated from Equation 3 (Schroeder and Deluca 1980):

$$N = \frac{DH(P_1 - P_0)\varepsilon A}{L} \qquad [3]$$

where N is the molar flux of the test gas (mol min^{-1}), D is the diffusivity constant ($\text{m}^2.\text{min}^{-1}$), H is the solubility coefficient (Henry's constant) for the gas-liquid system (mol kPa^{-1} m^{-3}), P_1 and P_0 are the upstream and downstream pressures (kPa), respectively, ϵ is the void fraction of the membrane (porosity), A is membrane's surface area (m2) and L is the effective diffusion length (thickness of the membrane materials) (m). Under actual operating or field conditions, diffusive airflow through an intact membrane can be significantly different from the theoretical values. In a recent study, Farahbakhsh & Smith (2003a) used a modified version of Equation 3 to estimate the diffusive flow rates for an intact membrane. Using a new term, κ, to account for the impact of pore tortuosity, membrane porosity, and effective diffusion length (L), the diffusive air flow rate (N, mol/min) through an intact immersed membrane was estimated by Equation 4:

$$N = \kappa DH(P_1 - P_0)A \qquad [4]$$

where, A is the membrane's surface area (m^2) , and κ (m^{-1}) is the membrane parameter and must be determined experimentally as it describes membrane's specific properties such as pore tortuosity, porosity and effective diffusion length. Using a bench-scale setup, κ was determined under applied pressures of 5 to 15 psi (35 to 100 kPa). The membrane parameter, κ, was found to be constant for membranes with different surface area at a specific applied pressure. Volumetric diffusive flow rates (in mL/min) can be then determined from Equation 4 using the ideal gas law as shown in Equation 5.

$$Q = \frac{NRT}{P} \qquad [5]$$

where Q is the diffusive air flow rates (mL/s), R is the universal gas constant (mL.atm/mol.K), T is the test temperature (K), and P is the downstream pressure (atm).

The value of diffusive airflow for an intact membrane as estimated by Equations 4 and 5 is quite small. In contrast, since oversize defects and holes have a much lower bubble point pressure, they allow the passage of larger volumes of air at a specified test pressure.

2.2.1.3 The Vacuum Hold Test

A variation of pressure decay test, that, for many years, has been used by the reverse osmosis industry for detecting leaks is referred to as the vacuum hold test (Nederlof et al. 1997; ASTM 1998). Recently, Kruithof et al (2001) applied the vacuum hold test for monitoring the integrity of UF membranes. They found that the vacuum hold test was quite sensitive in detecting minor leaks or integrity breaches in a hollow-fibre UF membrane.

The above pressure driven integrity monitoring tests may be affected by water temperatures, extent of membrane fouling, the extent of membrane wetting, and the membrane's surface area. In a recent study, (Farahbakhsh & Smith, 2003b) demonstrated that the impact of water temperature on diffusive air flow rates can be significant at very low temperatures, as shown in Table 2.1. Therefore, at very low water temperatures, the drop in diffusive air flow rate may mask the effect of a defect and prevent detection of the breech of membrane integrity. For this reason, Uhr (2001) suggested that, for cold waters, the criteria for determining membrane integrity should shift to accommodate lower diffusion rates. A membrane's surface area can also have a noticeable impact on the pressure driven integrity monitoring tests. An increase in a membrane's surface area results in a corresponding increase in diffusive airflow through the membrane. For membranes with very large surface areas, the increased diffusive airflow rates can mask measurements of airflow due to defects or oversized pores. In a full-scale study, Landsness (2001) showed that pressure decay test results were only significant after 6 out of 1.8 million fibres were cut. The results of pressure decay tests for less than six broken fibres were within the normal variations for the unit with no compromised fibre. This observation clearly indicates that the PD test looses its sensitivity for membranes with increasingly larger surface areas. It should be noted however, that 6 broken fibres out of 1.8 million represents a defect level of 0.00033 percent and may not seriously impact the log removal ability of a membrane with small fibre diameter.

Table 2.1 Influence of temperature on diffusive air flow rates through a wetted membrane (Source: Farahbakhsh & Smith, 2003b).

Temperature (°C)	Air diffusion/Air Diffusion$_{20}$°C
0	0.60
5	0.70
10	0.84
20	1.0
30	1.35

It is not quite clear what impact, if any, membrane fouling may have on the results of direct integrity monitoring tests. It has been shown that an increase in membrane fouling corresponds to an increase in the ability of UF and MF membranes to remove microorganisms (Adham et al. 1995; Jacangelo et al. 1995). This is primarily due to pore restriction, resulting in pore plugging, as well as increase resistance to flow caused by the fouling layer. It can therefore, be deduced that the presence of a fouling layer may partially mask the impact of a defect in terms of microbial passage. It is not clear however, whether or not the fouling layer reduces the sensitivity or reliability of direct integrity tests in signaling breach of membrane integrity. During a recent study however, Hong et al (2001) showed that membrane fouling had little to no effect on the sensitivity of pressure decay and diffusive airflow tests. Further work should, however, be conducted to verify the finding by Hong and coworkers.

Other factors that can affect the results of pressure-based integrity monitoring tests are the starting test pressure, the upstream volume, the extent by which a membrane is wetted, and the presence of other leaks in the system. Finally, the sensitivity of these tests is limited by the resolution of flowmeters or pressure sensors used (Meltzer 1992; Waibel et al. 1996).

One of the disadvantages of the above direct integrity monitoring methods is the need to perform the tests offline and the consequent interruption in the normal operation. Another limitation of pressure-driven direct integrity monitoring tests is the minimum detectable pore size that can be obtained under a typical range of test pressures. Using the bubble point equation (Equation 1) at $k = 0.25$ and $\theta = 45°$ (typical of commonly used membranes), the pressure required to detect a pore size of 0.1 μm (largest size virus) can be estimated to be 75 psi (520 kPa) (USEPA 2001). Considering that typical pressure for conducting PD or DAF tests is in the range of 10 to 20 psi (70 to 140 kPa), minimum detectable defects would be about 2 to 3 μm which would be adequate indication of the removal of protozoan cysts. To detect smaller size defects, higher test pressures are required which may be outside the operating range of most low-pressure membranes. Therefore, although direct pressure driven integrity tests can detect defects in size ranges equivalent to those of *Giardia* spp. and *Cryptosporidium* spp., they would be hard-pressed to detect defects that allow passage of bacteria and viruses. Despite these shortcomings, these methods are the most accurate techniques available for determining the integrity of low-pressure membranes. The shortcomings of these tests, however, highlight the need for standard procedures in conducting direct integrity tests for the water industry. Whereas standard guidelines are available for direct integrity testing of sterilizing UF membranes (Cole et al. 1996), no standard guidelines exist for conducting direct integrity testing of water treatment membranes. Currently, the American Society for Testing Materials (ASTM) is developing a new set of standards for monitoring the integrity of low-pressure membranes (Côté 2002). In addition, the proposed USEPA Guidance Manual for Membrane Filtration will be another step towards the development of such standard guidelines.

2.2.1.4 Acoustic Sensing

Acoustic sensors have been used by several researchers (Adham et al. 1995; Johnson 1997; Laine et al. 1998) as a means of diagnostic testing of membrane integrity. This method utilizes the hydrophonic sensor technology and monitors the increase in noise resulted from the flow of liquid under operating pressures through a hole or a defect. Laîne and co-workers (1998) successfully utilized a novel acoustic sensor for monitoring of a UF pilot system operated in dead-end mode and demonstrated that one compromised fibre could cause an increase in acoustic level of up to 20 dB. However, they found that continuous acoustic detection greatly depended on the background noise. In a membrane system operated in re-circulating mode, the noise generated by the re-circulating pump drowned the noise from the compromised fibre. Adham and co-workers (1995) discovered that the acoustic sensors needed to be placed at several locations in a module to effectively distinguish the sound generated by the defective fibre(s). Johnson (1997) recommended using the acoustic sensing method for isolating modules with damaged fibres once the overall integrity of a membrane array has been evaluated by other direct monitoring methods. To the knowledge of the authors, at least one membrane manufacturer utilizes a similar type of sonic testing device, to identify the membrane module with compromised fibre(s). This is done manually by the operator once the lack of integrity of a membrane array has been determined by the DAF or PD tests.

2.2.1.5 Microbial Challenge Tests

Direct integrity monitoring tests are meaningful only if they can be related to specific retention of microorganisms by the membrane. Membrane retention capabilities can be validated by conducting microorganism challenge tests. Extensive work has been conducted in the pharmaceutical industry to correlate microbial retention with the results of commonly used direct integrity monitoring tests. Most work in this field has focused on sterilizing membranes with pore sizes ranging from 0.2 to 0.45 μm. Most challenge studies with pharmaceutical grade filters have been conducted with *Pseudomonas diminuta* at challenge concentration load of about 10^7 organisms/cm^2 (Carter 1996; Cole et al. 1996). Johnson (1979) plotted correlations between microbial retention data and corresponding bubble point values for three different studies. All three groups of data produced straight lines of the same slope on a logarithmic scale, resulting in Equation 6 for microbial retention.

$$R = me^{aB} \qquad [6]$$

where R = the microbe reduction value, B = the bubble point pressure of the membrane (psi), a = the constant that reflects the method of measuring the bubble point and the kind of microbes involved, and m = slope of the line. From Equation 6, it is possible to predict the log reduction values of a microfilter if its bubble point pressure is known. Similar work by Leahy (1978) and Reti (1979) confirmed the results established by Johnson (1979). All plots produced a straight line with a slope of two, indicating the strong dependence of microorganism retention capability of a microfilter to its bubble point pressure (Jornitz et al. 1998). Another model presented by Johnson (1998) predicts log removal of particles (including microorganisms) greater than 0.2 μm. The model assumes that all particles (>0.2 μm) are rejected completely by an intact microfilter and that the portion of flow that passes through a defective fibre has the same concentration as that of the feed. The models related the log removal values (LRV) of a microfilter (pore diameter of 0.2 μm) to results of pressure decay and diffusive airflow tests as shown in Equations 7 and 8 (Hong et al. 1998):

$$LRV = \log\left[\frac{Q_{filt} P_{atm}}{V_{filt}} \frac{\mu_{water} (P_{test}^2 - P_{atm}^2)}{2\mu_{air} P_{filt} P_{atm}} \left(\frac{t}{\Delta P}\right)\right] \qquad [7]$$

$$LRV = \log\left[\frac{Q_{filt}}{Q_{DAF}}\frac{\mu_{water}(P_{test}^2 - P_{atm}^2)}{2\mu_{air}P_{filt}P_{atm}}\right] \quad [8]$$

where, Q_{filt} is filtrate flow rate (L/min), Q_{DAF} is air flow rate from DAF test result (L/min), μ_{water}, μ_{air} are viscosity of water and air respectively (kg/m.s), P_{test}, P_{filt}, and P_{atm} are test air pressure, transmembrane pressure and atmospheric pressure (kPa), respectively, V_{filt} is filtrate pipework volume (L) and $\Delta P/t$ is pressure decay rate (kPa/min). In a more recent work, Hong (2001) attempted to establish correlations between microbial removal efficiency of a pilot-scale microfilter and results of direct integrity monitoring tests (pressure decay and diffusive airflow tests). *Cryptosporidium spp*. oocysts, E. *coli* (ATCC 25922), and *Bacillus subtilis* spores were used for microbial challenge tests. Both direct integrity monitoring tests proved to be quite sensitive in detecting even one broken fibre. However, neither of the integrity monitoring techniques showed a statistically reliable correlation with microbial removal efficiency of the microfiltration system.

Spores of *Bacillus subtilis* and *Bacillus megaterium* have been used as surrogates to *Cryptosporidium* spp. oocysts during microbial challenge studies with low-pressure membranes (Trimboli et al, 2001; Côté et al, 2003). Using *Bacillus megaterium* spores in a 36 ML/d (9.5 mgd) water treatment plant, Trimboli and coworkers were able to verify greater than 5.9 log removal for a full-scale microfiltration plant. Their results indicated that, under most conditions, the theoretical LRV calculations (Equations 7 and 8) provided a conservative estimate of log removal capability of the microfiltration membrane. Their work also demonstrated that, due to substantial logistics of conducting spore challenge studies, spore challenge tests may not be a practical method for routine monitoring of membrane integrity. Côté et al (2003) challenged a pilot-scale immersed membrane with *Bacillus subtilis* spores and measured greater than 7 log removal by the intact membrane. The authors also showed that a theoretical relationship similar to Equation 7 produced conservative estimates of LRV for both an intact and a compromised membrane. Correcting for pressure decay rate (PDR), as shown in Equation 9, resulted in more accurate estimates of LRV for the immersed membrane.

$$PDR_{corrected} = PDR_{measured} - PDR_{Diffusion} \qquad [9]$$

Where $PDR_{diffusion}$ is the pressure decay rate for an intact membrane resulting only from diffusion.

2.2.1.6 Application of latex microspheres

Latex microspheres of a specific size may be used as surrogates for occasional challenging of membranes. Latex microspheres can be obtained in variety of sizes, charges and fluorescent water insoluble dyes. Neutral latex microspheres were used by Bower (1986) to develop a correlation between direct integrity tests and retention of microspheres by a 0.1-μm membrane filter. The authors however, were unable to develop a significant correlation between these parameters. Acker (2001) attempted to assess the integrity of reverse osmosis (RO) spiral-wound membranes with microspheres in a similar size range as that of MS2 phage (0.025 μm). They found that retention of latex microspheres by the RO membranes followed the same pattern as MS2 phage. However, a direct correlation could not be established between the retention of latex microspheres and MS2 phage. Use of latex microspheres as surrogate indicators for pathogenic organisms is still in the early stages of development. Some factors that may limit the application of latex microspheres are the difficulty associated with their detection at very low levels and the relatively high application costs.

2.2.1.7 The spiked integrity monitoring method

Another integrity monitoring method which has been recently introduced by Norit/X-flow (Franklin et al. 2000) involves periodic spiking of the feedwater with powdered activated carbon (PAC) of specific size range (70% of particles with less than 1.7 μm diameter) while monitoring the permeate with a particle counter. Earlier research by Glucina (1997) showed that the addition of PAC to the feedwater increased the sensitivity of particle counters for detecting lack of membrane integrity by increasing feed particle counts. This method of integrity monitoring was referred to as the spiked integrity monitoring system (SIM) by Van Hoof (2001) and has been used in at least one full-scale membrane plant with promising results (Franklin et al. 2001). The method showed increased sensitivity as compared with particle counting without spiking, as well as a better ability to estimate log removal of particles.

2.2.2 Indirect integrity monitoring techniques

Indirect membrane integrity monitoring techniques rely on monitoring a surrogate parameter such as turbidity, particle count or particle index in the permeate. These methods are not a direct indication of presence of holes or defects but can alert the operator of a possible breach in membrane integrity. Current indirect integrity methods include particle counting, particle monitoring and turbidity monitoring.

2.2.2.1 Particle counting

Particle counting has so far been the most promising means for indirect monitoring of the integrity of low-pressure membranes. A comprehensive evaluation of the indirect monitoring techniques was performed by Adham (1995), where they investigated the feasibility of turbidity monitors, particle counters and particle monitors with four different membrane pilot plants. Particle counting was shown to be the most sensitive of all indirect monitoring techniques. However, dilution ratio (ratio of total permeate flow from the intact fibres to that from the compromised fibres) seemed to have a strong impact on the sensitivity of particle counting in detecting breach of membrane integrity. It was found that higher dilution ratios resulted in lower sensitivity of the particle counting in monitoring membrane integrity. Other researchers (Glucina et al. 1997; Panglisch et al. 1998) also evaluated the use of particle counters for indirect monitoring of membrane integrity. Both investigators demonstrated that the sensitivity of particle counters for monitoring membrane integrity was a function of feed particle concentration and membrane surface area. Glucina and co-workers (1997) showed that particle counter's sensitivity in detecting a compromised fibre increased with increasing feed particle concentrations and decreasing membrane surface area. Panglisch and co-workers (1998) found that using a very sensitive particle counter (detection range from 0.05 to 0.2 μm) increased the sensitivity of integrity monitoring. The disadvantages of using highly sensitive particle counters were higher cost and the need for more complex controls to ensure the accuracy and precision of the particle counter. Both investigators recommended the use of mathematical models to determine, based on feed characteristics (e.g. feed particle counts) and operating conditions (e.g. recovery), the required sensitivity of the counters and the maximum surface area of the membrane that can be monitored by one counter. Mourato (1998) investigated the role of particle counters for on-line integrity monitoring of an immersed membrane system. During a full-scale investigation, they found that one particle counter was quite sensitive in detecting breach of integrity caused by three compromised fibres in a system with 4,407 m^2 of membrane surface area. The higher sensitivity of particle counting in this case can be attributed mainly to the larger fibre diameter of the membrane tested. Generally, higher flow through a broken fibre with a larger inside diameter results in the passage of higher number of particles. This higher number of particles can be more readily detected by an online particle counter. Figure 2.4 shows the result of indirect integrity monitoring using a particle counter on a membrane pilot plant with 4700 fibres.

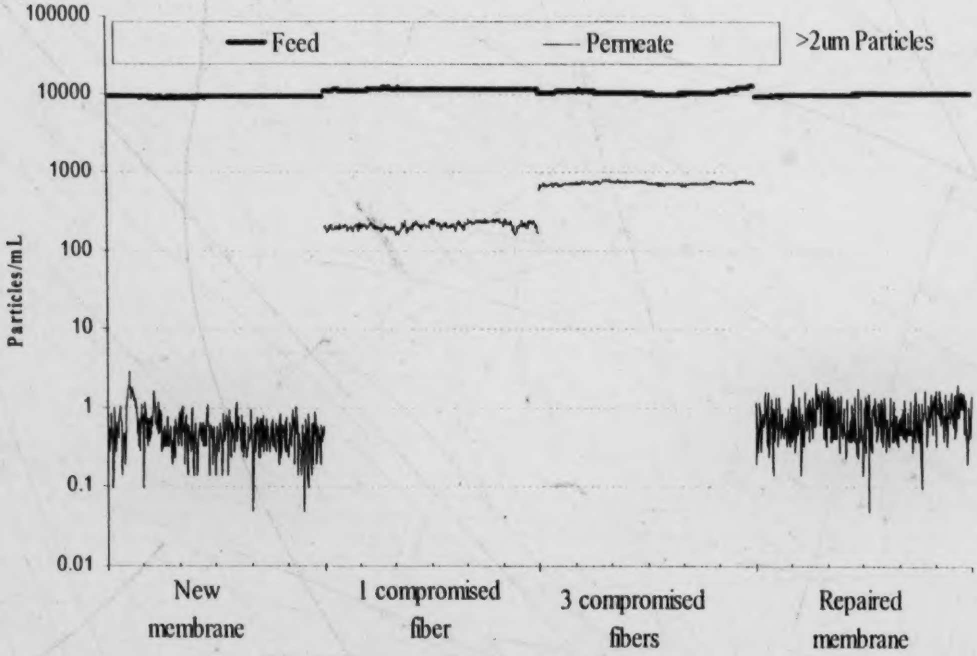

Figure 2.4. Results from an indirect integrity monitoring test using an online particle counter on a membrane with 4700 fibres (Source: Adham & Gramith, 1999b).

These results were used to estimate the maximum number of modules (60 modules in this case) that can be monitored by one particle counter to detect one compromised fibre. In another study, Kruithof (2001) compared the performance of two particle counters with different resolutions (0.05 μm and 1 μm) for monitoring the integrity of an UF water treatment system. They showed that both particle counters produced comparable results. The authors selected the 1 μm particle counter for online monitoring of the UF membrane integrity. The 0.05 μm particle counters were used for additional quality checks. The authors indicated that this method of integrity monitoring was quite reliable for up to 5 log units monitoring of the low-pressure membrane systems. One of the hindrances to the effectiveness of particle counters in monitoring membrane integrity is the potential for false positive readings caused by the presence of air microbubbles in the permeate. Microbubbles may enter the permeate after backwashing or during normal operating cycle. Membranes using air for backwash and those operating under suction are most susceptible to the presence of microbubbles.

A recent advance in particle counting is the development of multi-sensor particle counters. The development of these particle counters was an attempt to reduce the overall cost of conducting online membrane integrity monitoring for a large plant. These multi-sensor particle counters consists of up to 50 sensors that are operated via a central control system. All 50 sensors share the same light source, detector and control electronics to reduce the monitoring cost. Banerjee (2001) applied such a technology to monitor the permeate water quality in a membrane pilot plant. They demonstrated that the instrument had the sensitivity to detect some variations in the baseline particle count measurements. However, the multi-sensor particle counters require further development before they can be confidently used for online integrity monitoring of low-pressure membranes.

2.2.2.2 Particle monitoring

Particle monitoring is a relatively new technology for detecting the presence of particles in the permeate. Presence of particles is measured by the "particle index" which is set to vary from 0 to 4000 (or higher). It has been shown that there is a significant correlation between particle index and particle count (Kirby et al. 1998).

Adham and coworkers (1995) evaluated particle monitors for membrane integrity monitoring. Particle monitoring was shown to be less sensitive in detecting breach of membrane integrity than particle counting. Similar results were achieved by Glucina et al (1997), where they showed that particle monitoring lacked sufficient sensitivity when used to evaluate the integrity of UF and MF in both dead-end and cross-flow filtration modes. The sensitivity of particle monitoring was similar to that of a conventional turbidity monitor. At the present, particle monitoring is not suited for integrity monitoring due to its lack of sensitivity. In addition, recent declines in the cost of particle counters have made particle monitoring less attractive as an indirect integrity monitoring technique.

2.2.2.3 Turbidity monitoring

Turbidity monitoring using conventional turbidimeters has shown to be ineffective in detecting minor breach of membrane integrity ((Adham et al. 1995; Glucina et al. 1997; Colvin et al. 2001; Landsness 2001). This is mainly because most water treatment membranes consistently produce water with very low turbidity, despite breaches in membrane integrity. However, the recent development of highly sensitive laser turbidimeters (0.02 to 0.001 ntu) has given a new impetus to the use of turbidity meters for online and continuous monitoring of membrane integrity. Colvin (2001) compared the performance of a laser turbidimeter with other methods of monitoring the integrity of MF and UF membranes including pressure decay test and particle counting. Their investigation revealed that, under pilot-scale operations, particle counting was more effective in detecting the breach of membrane integrity than a laser turbidimeter. Laser turbidimeters should be studied under full-scale operations so that a more realistic evaluation of the effectiveness of this method can be conducted. Figure 2.5 shows the results of turbidity monitoring for a membrane with 20,000 fibres. Turbidity monitoring was unable to detect small numbers of broken fibres.

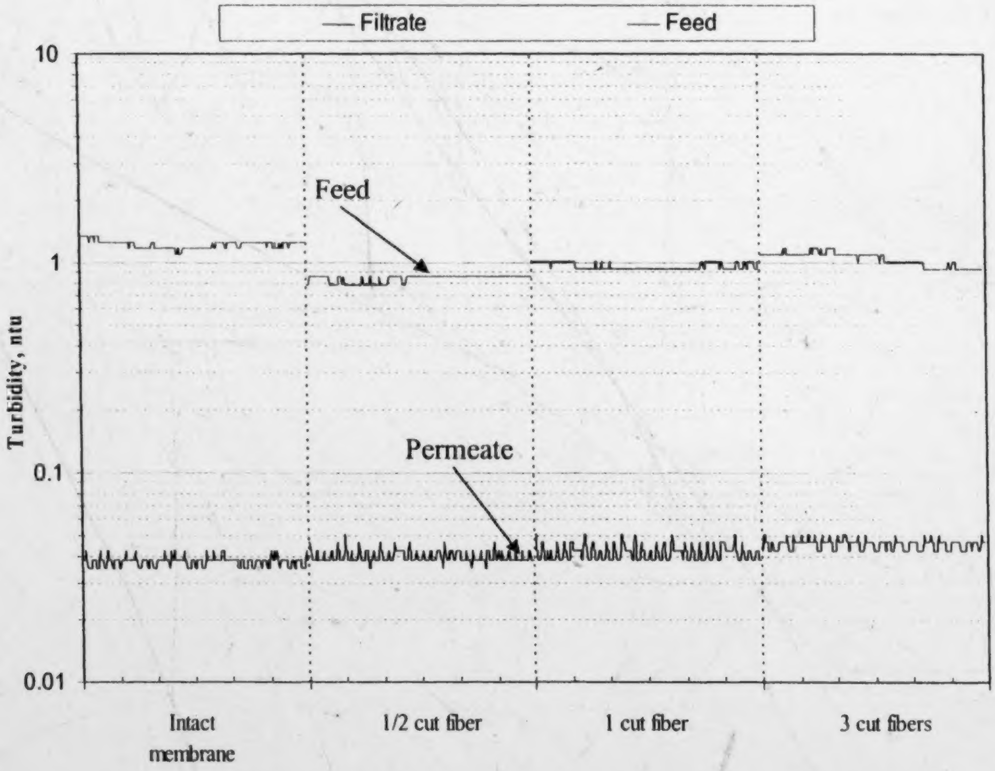

Figure 2.5 Indirect integrity monitoring with an online turbidimeter for a membrane with 20,000 fibres (Source: Adham et al, 2001).

Although some of the indirect integrity monitoring techniques have produced promising results, they have several limitations that must be addressed. Most indirect integrity monitoring techniques are affected by the feed water quality, operating conditions (transmembrane pressure and permeate flux), mode of membrane operation (dead-end vs. crossflow, inside-out vs. outside-in), membrane surface area, fibre's inside diameter, and membrane fouling. Other factors affecting the results of indirect monitoring tests relate to the instruments used during the tests. Instrument sensitivity and proper calibration and operation can significantly impact the results of integrity monitoring tests. In addition, none of the indirect monitoring tests have been correlated with microbial removal. A better knowledge base must be developed for these technologies and further research is needed before indirect monitoring techniques can become an acceptable component of membrane integrity monitoring.

2.3 THE SEARCH FOR AN IDEAL MEMBRANE INTEGRITY MONITORING TECHNIQUE

The American Water Works Association Research Foundation (AWWARF) established five criteria for an ideal integrity monitoring technique (AWWARF 2000). These criteria included continuity, sensitivity, reliability, identifiability, and economy. According to AWWARF, an ideal membrane integrity monitoring test should be performed on-line and in a continuous fashion, must be able to detect small breaches in membrane integrity under full-scale operations, should not produce false negative or false positive signals, should be able to identify the individual compromised fibres, and must be economically feasible. To the above criteria, one can add the requirement for the integrity monitoring test to be meaningful in terms of microbial reduction, ease and simplicity of operation, and applicability to a wide range of membrane configurations, feed water characteristics and operating conditions. The development of such an integrity monitoring test may prove to be extremely difficult. Table 2.2 summarizes advantages and disadvantages of existing integrity monitoring tests. A comprehensive summary is also available in USEPA (2001). Most direct methods, although sensitive and reliable, cannot be used continuously and can be labor intensive. While indirect monitoring techniques that can be used continuously, they lack sensitivity, reliability and the ability to isolate the compromised fibre. Only one technique, the bubble point test, can identify the compromised fibre while certain techniques seem to be more applicable to a specific type of membrane and/or certain operating conditions. The search for an ideal integrity monitoring test, therefore, may well result in the development of an integrity monitoring protocol that combines several of the existing or new techniques into a comprehensive program. Currently the membrane water treatment industry's standard test for detecting minor breaches of membrane integrity is the pressure hold (decay) test, while particle counting and/or turbidity monitoring are used to meet regulatory requirements and to detect more pronounced breaches of membrane integrity. Figure 2.6 shows the results of an online integrity monitoring using a turbidimeter in which a major breach of membrane integrity (over 60 broken fibres out of 28,500 fibres) was detected.

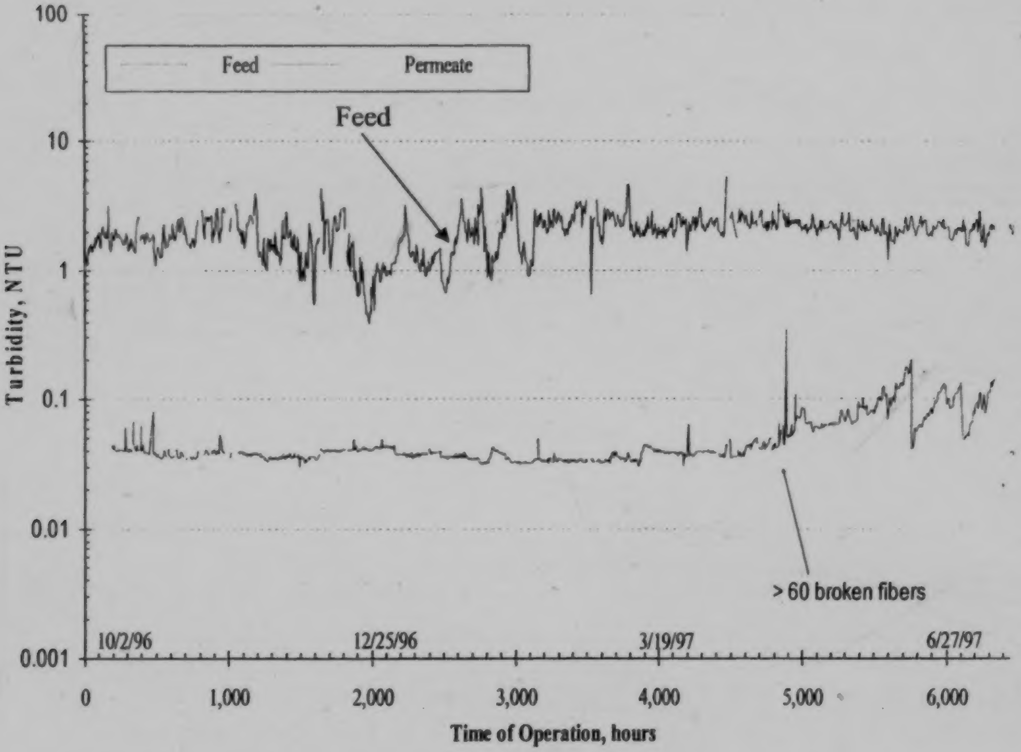

Figure 2.6 A major breach of membrane integrity was detected with an online turbidimeter (Source: Gagliardo et al, 1997).

Table 2.2. Summary of advantages and disadvantages of existing integrity monitoring tests.

	Method	Advantages	Disadvantages
Direct Methods	Bubble Point Test†	• Identifies individual compromised fibres • Reliable and easy to interpret • Follows a relatively standard procedure	• Time consuming and labour intensive • Has to be preformed offline • Cannot monitor integrity of the entire system or a module • Can be subject to operator's error • Has to be used in conjunction with other direct methods

Method	Advantages	Disadvantages
Pressure Decay Test	• Can be used to monitor the integrity of a number of modules at once • Is highly automated • Is an accepted standard test for most membrane suppliers • Can detect small breaches of membrane integrity • Can be performed relatively quickly • Can reveal leaks in downstream plumbing	• Must be performed offline • Lacks a standard procedure • Requires a fully-wetted membrane • Lacks a reliable base-line value • Difficult to correlate with log removal values (LRV) • It is not continuous • Results affected by many factors including temperature, instrument sensitivity, upstream volume, etc. • It is prone to dilution effects
Vacuum Decay Test	• Similar to the pressure decay test although not widely used by membrane suppliers	• Similar disadvantages to the PDT • It is not fully developed and proven • Requires additional tank for water trap • More difficult to conduct
Diffusive Flow test	• Similar to pressure decay test • Can be more accurate if volume displacement measured • It is reportedly more sensitive than PDT	• Similar to PDT • Currently not fully automated • Currently not supplied as standard equipment
Sonic Sensing Test†	• Can identify compromised modules • Could be developed into a continuous test • Relatively easy to use	• Not automated • May be affected by background noise or mode of operation • Interpretation of results may be subjective • Not widely used • Time consuming and labour intensive • Cannot be used with submerged systems
Spiked Integrity Monitoring Method	• Can be performed more frequently than other direct methods • May provide a relatively good indication of LRVs • Relatively easy to use • Have shown reasonable sensitivities	• Still under development • Not widely used • Require addition of a surrogate • Continuous tests may be difficult and expensive • Relatively difficult to establish a baseline value • Prone to interference from other particles naturally present in water

	Method	Advantages	Disadvantages
Indirect Methods	Particle Counting	• Performed continuously • Widely used and usually a standard equipment • Shown to be more sensitive than other indirect methods • May be used in multiple channel configuration to save cost	• May not detect minor breaches of membrane integrity • Affected by changes in raw water particle counts – Difficult to establish a baseline value • Requires difficult and frequent calibration • Can produce false positives if microbbubles are present in permeate or due to particle shedding in the plumbing • Requires regular maintenance and cleaning of the sensor • Test results depends on the resolution of the instruments • Precision varies between different instruments • Can be relatively expensive specially for larger plants
	Particle Monitoring	• Performed continuously • Has lower costs than particle counters • Requires little to no calibration • Has higher sensitivity than conventional turbidimeters	• Less sensitive than particle counters • Can produce false positives if microbbubles are present in permeate or due to particle shedding in the plumbing • Does not provide particle counts or sizes only a relative index • Results harder to interpret than particle counters • The sensor may clog
	Turbidity Monitoring	• Performed continuously • A standard equipment in nearly all surface water treatment plants • Lower cost than particle counters • The new laser units may provide increased sensitivity	• Relatively insensitive to small breaches in membrane integrity • Requires regular maintenance and calibration • Can produce false positives if microbbubles are present in permeate or due to particle shedding in the plumbing

† Has been proposed as a diagnostic test.

2.4 RECENT ADVANCES AND FUTURE DIRECTIONS

Recent advances in monitoring devices have greatly improved the possibility of developing effective membrane integrity monitoring techniques. Development of more sensitive pressure transducers and gas flowmeters for example, has improved the reliability and sensitivity of direct integrity monitoring techniques. Higher resolution particle counters and turbidity monitors have increase the sensitivity of indirect integrity monitoring techniques. Attempts to reduce the cost of monitoring have resulted in more economical particle counters and turbidity monitors. Despite recent advances, there are still several areas in the integrity monitoring field that require further research and development. The available direct integrity monitoring techniques are time consuming and in some cases require draining of the membrane tanks and vessels. None of these tests can be performed continuously and as yet, no standard procedure is available for conducting these tests. The indirect monitoring techniques, although continuous, still lack sufficient sensitivity and are affected by variations in operating conditions and, in some cases, the presence of air bubbles in the permeate. Reducing the overall cost of indirect integrity monitoring tests is still a challenge that must be successfully met before these techniques can gain widespread acceptance. Furthermore, the effectiveness and reliability of any of the available integrity monitoring tests depends on the reliability of the instruments that are used in conducting the tests. This includes effective and regular maintenance, calibration and troubleshooting of these instruments to ensure a reliable operation. Finally, the search for the ideal integrity monitoring technique may be an elusive one. The demand for reliability may necessitate the need for a comprehensive integrity monitoring program that involves more than one test. An integrity monitoring "index" may need to be developed that translates the results of several integrity monitoring tests into a comprehensive and easy to interpret means of monitoring the integrity of water treatment membranes.

2.5 SUMMARY AND CONCLUSIONS

Although MF and UF membranes can be considered absolute barriers for many microorganisms of interest to the water treatment industry, the potential for breach of membrane integrity and its effect on microbial reduction highlights the need for sensitive and reliable integrity testing. Currently, various techniques are available for direct or indirect monitoring of membrane integrity. Direct integrity monitoring methods include the bubble point test, the pressure hold (decay) test, the vacuum hold (decay) test, the diffusive airflow test, the sonic test and the spiked integrity monitoring. Particle counting, turbidity monitoring, and particle monitoring are among the indirect integrity monitoring techniques. Currently, no single integrity monitoring test is available that fulfils all integrity monitoring requirements. An integrity monitoring program, therefore, needs to be developed that incorporates several of the existing tests into a comprehensive program for detecting breaches in membrane integrity. This program may include the following components:

1. establishing log removal values for a specific membrane filtration product using challenge studies with either microorganisms of interest or surrogate organisms;

2. conducting continuous indirect tests, such as particle counting, to detect major breaches of membrane integrity;
3. conducting less frequent direct tests, such as the PD test, to detect minor integrity breaches;
4. using theoretical relationships to estimate log removal values for a specific system based on results from direct tests; and
5. conducting diagnostic tests, such as acoustic tests, and bubble point test to identify compromised modules or fibres.

The current practice in the membrane water treatment industry is the use of pressure hold (decay) tests for detecting minor breaches of membrane integrity, while particle counting and/or turbidity monitoring are used to meet regulatory requirements and to detect more pronounced breaches in membrane integrity.

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CHAPTER 3. ESTIMATING AIR DIFFUSION CONTRIBUTION TO PRESSURE DECAY DURING MEMBRANE INTEGRITY TESTS*

3.1. INTRODUCTION

The rapid growth of low-pressure water treatment membranes in the past decade has been spurred mainly due to their ability to remove protozoa and bacteria in surface waters. Complete removal of coliform bacteria, *Giardia* spp. and *Cryptosporidium* spp. by microfiltration (MF) and ultrafiltration (UF) membranes has been reported by several researchers (Jacangelo et al. 1991; Adham and Jacangelo 1994; Freeman et al. 1996; Hirata and Hashimoto 1998). A compromised membrane, however, may no longer be an effective barrier against microorganisms. Presence of defects, oversized pores and broken fibres may lead to passage of pathogenic microorganisms and their entry into the public water supplies. For this reason, effective monitoring of the integrity of low-pressure membranes is of outmost importance and has been the topic of much research in the past few years. Increasing numbers of regulatory agencies in North America and Europe require membrane water treatment utilities to conduct some form of integrity monitoring, on a regular basis.

Over the past two decades, the membrane water treatment industry has developed various techniques for monitoring the integrity of low-pressure membranes. The most widely used membrane integrity monitoring tests is currently the pressure decay or pressure hold test. Diffusive air flow test is another pressure-driven integrity monitoring test that is used to a lesser degree by some membrane manufacturers. A detailed review of current integrity monitoring tests is provided elsewhere (Farahbakhsh et al. 2003).

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* A version of this Chapter was submitted for publication to the Journal of Membrane Science, April 2003.

The basis of all pressure-driven integrity monitoring tests is founded on the bubble point pressure concept. Briefly, when the upstream of a wetted membrane is pressurized with air or another test gas (i.e. Nitrogen); the test gas tends to diffuse through the water filled pores of the membrane and exit at the downstream side of the membrane. As air pressure is increased, larger volumes of air are transferred to the downstream side. At a certain pressure, commonly referred to as the bubble point pressure, water vacates the largest pore(s) and air passes freely through the emptied pore(s), giving rise to the passage of larger volumes of air. The bubble point pressure can be related to the diameter of the largest pore or defect as given in Equation 1:

$$P_B = \frac{4k\gamma Cos\ \theta}{d} \qquad [1]$$

where P_B is the bubble point pressure (Pa), k is the correction factor for the shape of the largest pore, γ is the surface tension of the wetting liquid in ($N.m^{-1}$), θ is the contact angle between the liquid and the membrane, and d is the diameter of the largest pore (m). A pressure decay or diffusive flow test is typically conducted at pressures below the bubble point pressure of an intact membrane. The upstream side of a wetted membrane is pressurized with air to a specific pressure and the pressure source is isolated. The lack of membrane integrity is signalled, if the rate of pressure loss or air flow is above an acceptable value.

It has been shown however, that the effectiveness of the pressure decay test in detecting breech of membrane integrity is affected by the membrane's surface area. This phenomenon, sometimes referred to as the "dilution effect", becomes more prominent as the membrane's surface area increases. For example, in one study, pressure decay tests on a membrane with 90 modules did not reveal lack of membrane integrity until six fibres were cut; whereas, in another study, the pressure decay test was much more sensitive when applied to only one rack of the same membranes (USEPA 2001).

Loss of pressure during a pressure-driven direct integrity test results either from the diffusion of air through the wetted membrane pores or due to bulk flow of air through an oversized pore or defect. The amount of air that diffuses through a wetted membrane at a certain applied pressure is a function of membrane's overall porosity (ϵA), where ϵ is the membrane porosity and A is membrane's surface area. Therefore, during a pressure decay test, an oversized defect or hole can produce the same result as an increase in membrane's overall porosity. Often, air flow rate due to diffusion through intact pores can be significantly larger than air flow rate through an oversized pore, especially for membranes with very large surface area (high overall porosity). Diffusion airflow can therefore act as a background noise during a pressure-driven direct integrity test, thereby masking the effect of oversized pores or defects. This can produce false-positive or false-negative results. Therefore, estimating and accounting for the contribution of air diffusion to pressure decay during a pressure decay test would produce much more reliable and sensitive results.

This paper presents the development of a predictive model for estimating the diffusive air flow rate through a wetted intact membrane and its contribution to pressure decay.

3.2.. THEORETICAL DETERMINATION OF DIFFUSIVE AIRFLOW

The Fick's law of diffusion may be used to estimate the flow of air due to diffusion through water-filled pores of an intact membrane. The Fick's law for an intact membrane can be written as follows:

$$N = \frac{D(C_1 - C_0)}{L} \varepsilon A \qquad [2]$$

where,

N = the molar flow of diffused air, mol.s^{-1};

D = the diffusivity constant for the air-water system, m^2.s^{-1};

ϵ = the void fraction of the membrane (membrane porosity);

L = length of diffusive path which is equal to the wall thickness for a hydrophilic membrane with cylindrical pores, m;

A = membrane's surface area, m^2; and

C_1 - C_0 = Concentration gradient for air across the wetted membrane, mol.m^{-3}.

Using Henry's Law, the term ($C_1 - C_0$) can be replaced with H ($P_1 - P_0$) and Equation 2 can be written as follows:

$$N = \frac{DH(P_1 - P_0)}{L} \varepsilon A \qquad [3]$$

where,

H = Henry's Law constant for the gas used, air in this case ($mol.atm^{-1}.m^{-3}$);

P_1 = the applied test pressure (atm); and

P_0 = the downstream pressure (atm).

The applied test pressure, P_1 is the arithmetic average of the initial test pressure (P_i) and the final test pressure (P_f) since the pressure drop typically follows a relatively straight line. In most cases, when conducting direct integrity tests, the downstream side is vented to the atmosphere; thus, the term ($P_1 - P_0$) can be replaced with term P, which represents the gage pressure.

It should be noted that in deciding to use diffusivity and Henry's constant for air in Equation 3, it is assumed that the two main constituents of air, N_2 and O_2, diffuse through the wetted membrane at the same rate. This however, may be somewhat of an oversimplification. The diffusivity constant for O_2 (as shown in Table 3.2) is slightly higher than N_2 (by about 1.3 times). The solubility of O_2 in water as determined by the Henry's constant is also higher than N_2 (by about 2 times). However, the mole fraction of N_2 in air is higher by almost 3.8 times than that for O_2. Therefore, under most circumstances, N_2 is expected to diffuse first by the virtue of its higher molar concentration. All of the above can get even more complicated if one accounts for the presence of water vapour in air. For the sake of simplicity and for purposes of the integrity test however, the general approach to Equation 3, which considers air as the main component of diffusion, is justified.

3.2.1 The Effective Diffusion Path (L)

Due to the technique used during the manufacture of most asymmetric membranes, the actual membrane wall thickness is unknown and, in fact, cannot be considered constant along the length of membrane fibres. The wall thickness for a polymeric membrane may also be affected by the applied pressures used during a direct integrity monitoring test. Therefore, it is difficult to closely estimate the membrane's wall thickness and hence the effective diffusion path (L). Another issue that contributes to the uncertainty regarding the actual length of the diffusive path is the extent by which different membranes are wetted. The extent of membrane wetting is somewhat related to the degree of membrane hydrophobicity and cannot be accurately quantified. Consequently, the term L, in Equation 3, should be treated as an unknown variable.

3.2.2 Impact of Pore Tortuosity on L

Membrane pores are seldom cylindrical and are often irregular, tortuous structures. A pore matrix for the ZeeWeed®500 hollow fibre membrane is shown in Plate 3.1. As shown, the membrane consists of interconnected, irregular and highly complex pore structures with tortuous flow paths. As a result of tortuosity of membrane pore structures, the effective length of diffusion path (L) is often larger than the thickness of membrane's wall. Tortuosity, therefore impacts the magnitude of diffusive airflow rate, with higher tortuosity resulting in lower diffusion rates. Pore tortuosity is an intrinsic characteristic of a specific membrane and is very difficult to measure. Its impact on diffusive flow however, can be significant and should not be ignored. Adding tortuosity (ζ) to Equation 3 and rearranging the terms results in the relationship given in Equation 4:

$$N = \left(\frac{\varepsilon}{\zeta L}\right) DH\,(P_1 - P_0)A \qquad [4]$$

In addition to tortuosity, membrane porosity (ϵ) is also difficult to determine accurately. The effective diffusion path (L), tortuosity and porosity may be combined together to represent the unknown components of Equation 4. The combined parameters are referred to hereafter as the membrane parameter which is represented by the term κ (m^{-1}). Replacing these three parameters with κ in Equation 4, results in Equation 5:

$$N = \kappa DH\,(P_1 - P_0)A \qquad [5]$$

The membrane parameter, κ, is an intrinsic characteristic of a membrane and may be considered constant for a specific membrane at a certain applied pressure. It must be established for a specific membrane experimentally.

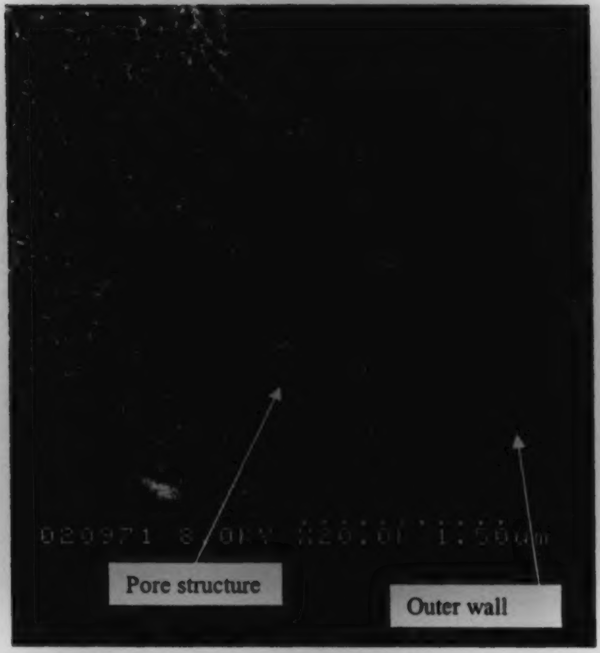
020971 8.0kV X20.0K 1.50um
Pore structure
Outer wall

Plate 3.1 Pore matrix of the ZeeWeed®500 hollow fibre membrane

3.2.3 Determining H for the Air-Water System

Values of H for the air-water system are presented in various forms in many reference materials. Perry's Chemical Engineer's Handbook (1984) provides the values for an air-water system as presented in Table 3.1.

Table 3.1. Henry's constant for the air-water system at various temperatures.

Temperature (^{o}C)	H (atm/x_i)	H† (mol.Pa^{-1}.m^{-3})	H† (mol.atm^{-1}.m^{-3})
0	4.32E+04	0.0127	1.2860
5	4.88E+04	0.0112	1.1384
10	5.94E+04	0.0092	0.9352
15	6.07E+04	0.0090	0.9152
20	7.20E+04	0.0076	0.7716
25	7.71E+04	0.0071	0.7205
30	8.23E+04	0.0066	0.6750
35	8.70E+04	0.0063	0.6385
40	9.11E+04	0.0060	0.6098
45	9.46E+04	0.0058	0.5873
50	1.01E+05	0.0054	0.5500

† Conversions by the authors.

3.2.4 Determining D for the Air-Water System

To determine the diffusion coefficient (D) for the air-water system, the following relationship can be used (Welty et al. 1984):

$$D_{(Air-water)} = \frac{1}{\sum \left({y'_f}/{D_{f-water}} \right)} \qquad [6]$$

where,

y'_f = mole fraction of each gas component, and

$D_{f\text{-}water}$ = diffusion coefficient of the gas component-water system.

Table 3.2 presents the above values for oxygen and nitrogen at 1 atm and 25^{o}C.

Table 3.2. Diffusion coefficients for O_2 and N_2.

Gas	Mole Fraction (y)	Diffusion Coefficient (D) ($m^2.s^{-1}$)
O_2	0.21	2.5×10^{-9}
N_2	0.79	1.9×10^{-9}

It should be noted that the above values hold true for dry air, but represent an acceptable estimation for the purpose herein. The diffusion coefficient, D is a function of temperature and can be related to temperature according to Equation 7 (Wilke and Chang 1955):

$$D_{O_2-H_2O} = 7.4 \times 10^{-8} \frac{T\left(\psi_{H_2O} M_{H_2O}\right)^{\frac{1}{2}}}{\mu V_{O_2}^{0.6}} \qquad [7]$$

where $D_{O2\text{-}H2O}$ is the diffusion coefficient for the oxygen-water system, T is the absolute temperature (K), ψ_{H2O} is an association parameter for water (2.6 for water), M_{H2O} is molecular weight of water (g/mol), μ is the viscosity of water (centipoises), and V_{O2} is the molar volume of oxygen (cm^3/g).

3.2.5 Impact of impurities on solubility

Dissolution of air in water is also affected by the presence of contaminants and salts in water. For natural water, therefore, an additional term should also be added to the Equation 5 to account for the presence of impurities. Equation 3 can then be written as follows:

$$N = \beta \kappa D H \ (P_1 - P_0) A \qquad [8]$$

where, β can be defined as the ratio of saturation concentration of air in natural water to the saturation concentration of air in pure water. Term β can be determined experimentally or using available relationships such as the Sechenov Salt Effect relationship. For pure water, β is considered to be 1.

3.2.6 Estimating Pressure Decay Rate Due to Diffusion

Once the diffusive airflow rate is known for a given membrane and assuming ideal gas behaviour for air, the pressure decay due to diffusion can be estimated from the relationship given in Equation 9:

$$PDR = [\beta \kappa D H (P_1 - P_0) A]\frac{RT}{V} \quad [9]$$

where,

PDR = pressure decay rate for a given membrane, atm.min^{-1}

κ = membrane parameter, m^{-1}

R = universal gas constant, 82.06 mL.atm.mol^{-1}.K^{-1}

T = temperature, K

V = the hold-up volume or pressurized volume, L.

3.3. MATERIALS AND METHODS

Two hollow fibre membrane modules with different surface areas, 0.21 and 0.09 m^2, were used during the experiments. These modules were constructed at the University of Alberta laboratories using ZeeWeed® 500 hollow fibres provided by Zenon

Environmental Inc. The membrane modules were constructed as 38 mm inside diameter pressurized units. De-ionized (DI) water was used during the entire experiment. The first step was to ensure that the membrane modules were intact by determining the membrane's bubble point pressure.

The setup for determining membrane's bubble point pressure is shown in Figure 3.1.

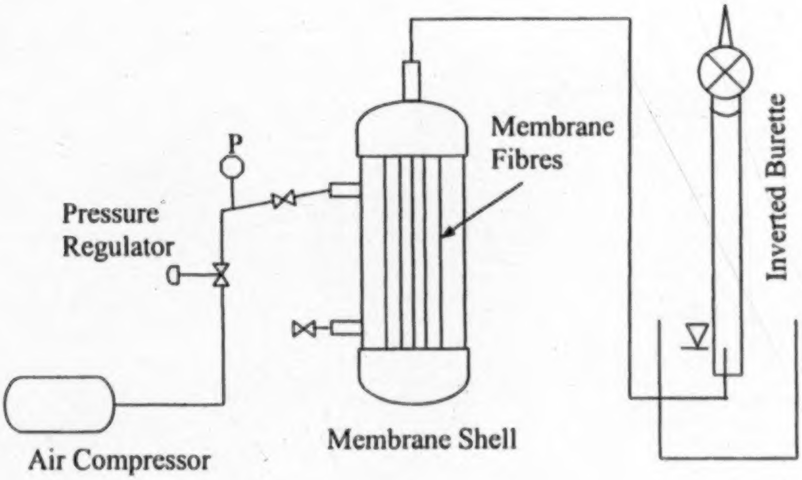

Figure 3.1 Schematic diagram for determining bubble point pressure.

The membrane's bubble point pressure was determined by measuring the diffusive flow through the wetted membrane, at increasingly higher pressures applied to the outside of the fibres. Bubble point pressure was then identified as the deflection point of the plot of the diffusive flow vs. applied pressure.

Once it was determined that the membrane was intact, diffusive air flow rates were measured for the wetted membrane while it was pressurized at 35 to 103 kPa (5 to 15 psi) from the inside of the lumens, as shown in Figure 3.2. The shell side was emptied of water and the permeate side of the wetted membrane was pressurized at 35, 70, and 103 kPa (5, 10, and 15 psi). Once the membrane was isolated from the air compressor, diffusive flow rates were measured using an inverted burette. Water temperatures were maintained at 20 ± 0.5°C during all runs. Upstream pressure was also measured using a pressure transducer and pressure data were collected during the entire runs using a LabView program. For each run, therefore, both diffusive air flow rate and pressure decay rate data were collected.

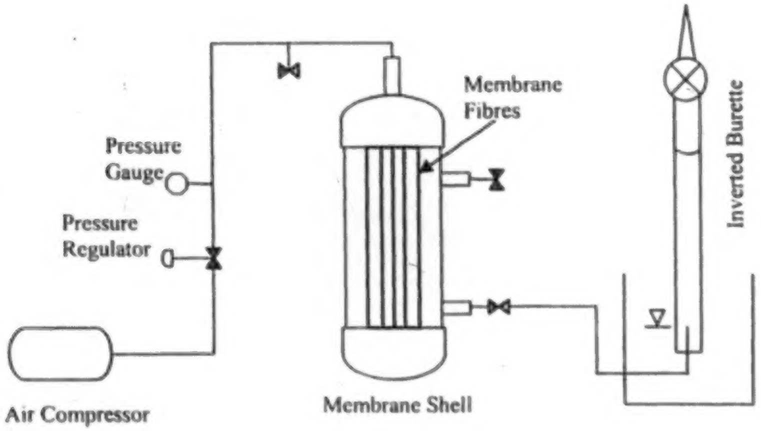
Membrane Fibres
Inverted Burette
Pressure Gauge
Pressure Regulator
Air Compressor
Membrane Shell

Figure 3.2 Schematic diagram for measuring the diffusive air flow rates.

3.4. RESULTS AND DISCUSSION

3.4.1. Bubble point pressure determination

Typical results of bubble point pressure measurement for the membranes with the same surface area are presented in Figure 3.3. The results indicated that the bubble point pressure for all intact membranes was around 480 kPa (70 psi), which corresponded to the bubble point pressure of a 0.1 μm PVDF membrane.

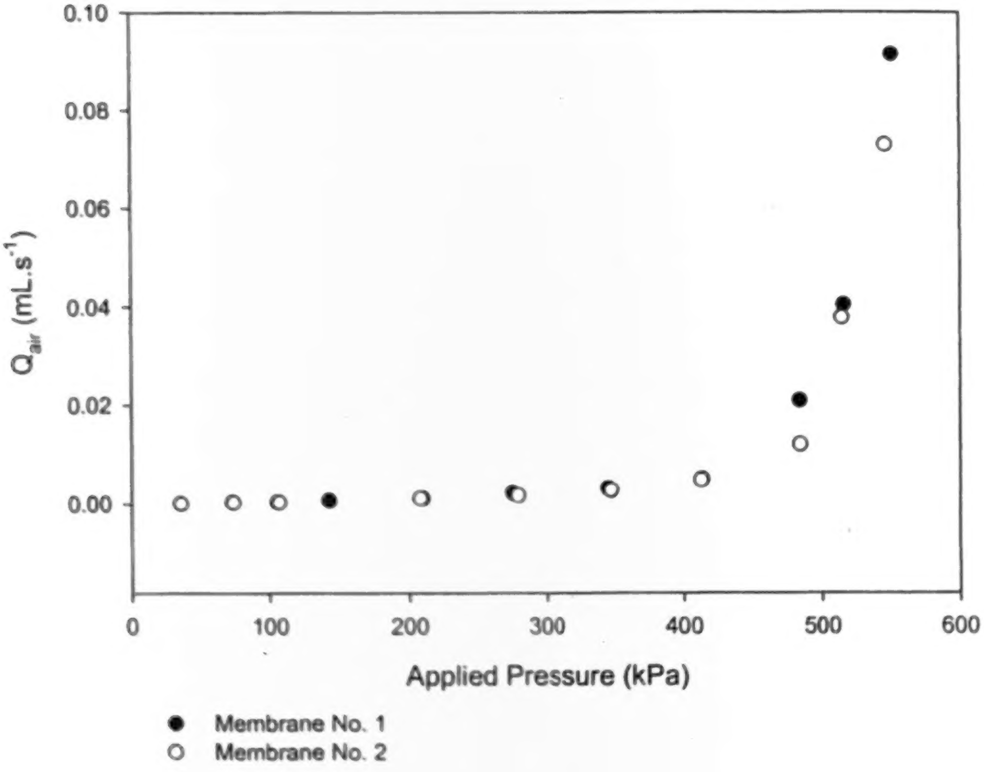

Figure 3.3 Results of bubble point pressure measurements for two of the membranes.

Figure 3.3 also illustrates that diffusive air flow rate for an intact membrane, at pressures below the bubble point pressure, seems to be a linear function of applied pressure. A closer look at the data however, reveals a different picture. Figure 3.4 demonstrates that beyond 103 kPa (15 psi), diffusive air flow is no longer a linear function of applied pressure. Deviation from linearity may be due to the fact that applied pressure affects the length of the diffusive path, porosity and tortuosity in a non-linear fashion. A similar phenomenon was also observed by an earlier researcher (Reti 1977) when he observed departure from linearity for the diffusive airflow curve at values below the bubble point pressure of a flat sheet microfilter. He showed that this behaviour was primarily caused by the thinning of the liquid layer in membrane pores or a reduction in the length of the effective diffusive path, as a result of higher applied pressures. However, for the bench-scale ZeeWeed® module, there seems to be a linear relationship between the diffusive flow and applied pressure in a range of 35 to 103 kPa (5 to 15 psi); this is the typical range of pressure during a pressure decay test. This is shown in Figure 3.5.

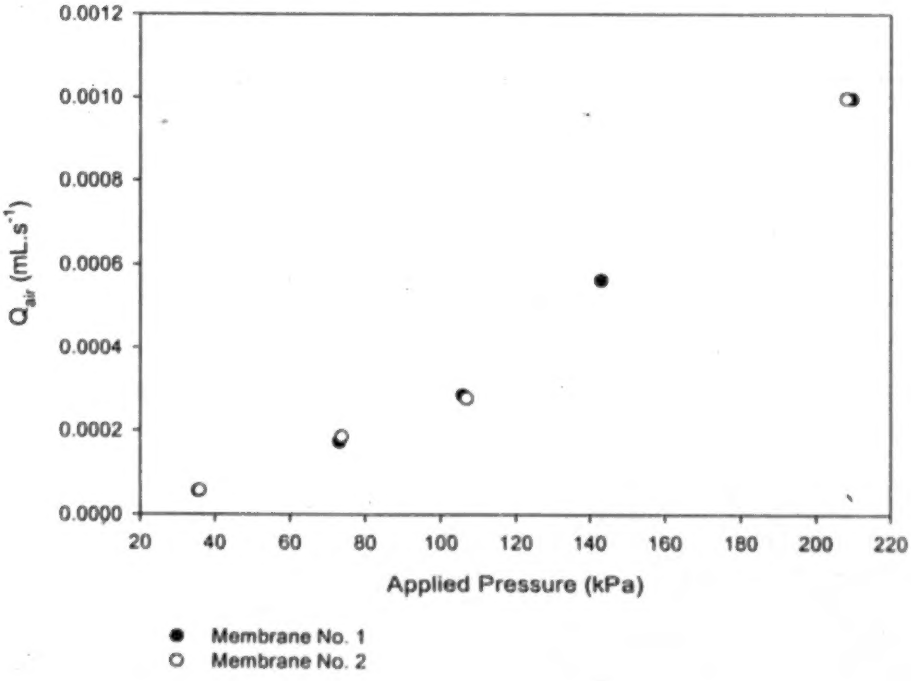

Figure 3.4 Non-linear relationship between diffusive flow and applied pressure beyond 103 kPa.

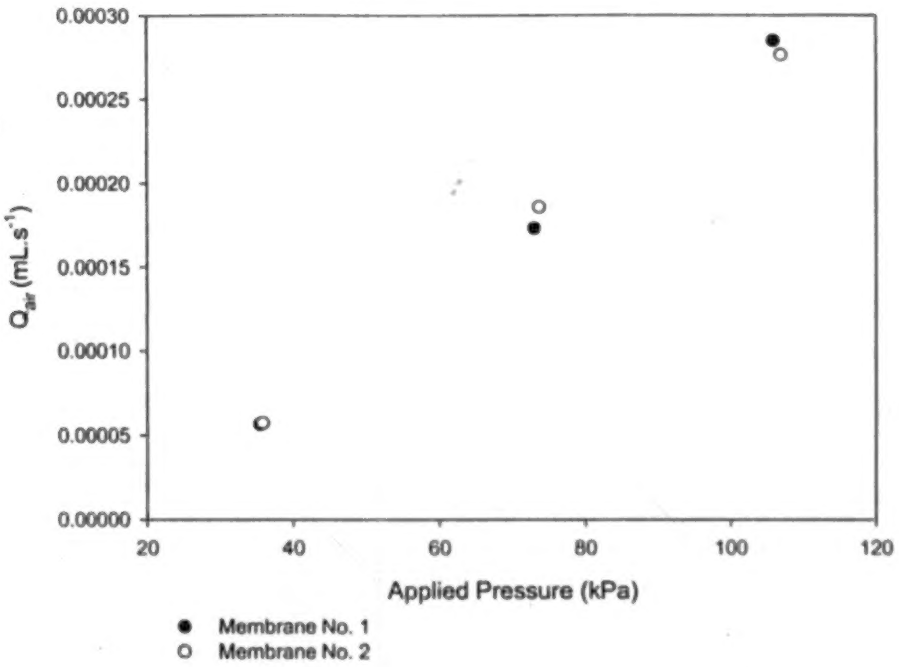

Figure 3.5 The relationship between diffusive air flow rates and applied pressure.

Consequently, based on Figure 3.5, the Fick's first law of diffusion can be used for estimating the air flow rates due to diffusion for an intact ZeeWeed®membrane.

It should be noted that a straight line through the data points shown in Figure 3.5 would not pass through the origin. This implies that below 35 kPa (5 psi), the slope of the diffusion line changes from that between 35 kPa and 103 kPa. A similar change of slope in the diffusive flow curve is apparent at applied pressures above 103 kPa. In fact, a diffusive air flow measurement at the test pressure of 14 kPa (2.0 psi) yielded a flow of 0.00032 mL.s^{-1}, resulting in a straight line curve from zero to 35 kPa (0 to 5 psi) but with a different slope. Consequently, the diffusive airflow model, which will be presented in subsequent sections, is valid only for the test pressures between 35 to 103 kPa (5 to 15 psi).

3.4.2. Determination of Diffusive Air Flow rates and the Membrane Parameter (κ)

At this stage of the study, diffusive air flow rates for membrane A (surface area of $0.09m^2$) was measured as described earlier, using the setup shown in Figure 3.2. All measurements were conducted using DI water at 20 ± 0.5°C. Results are shown in Figure 3.6.

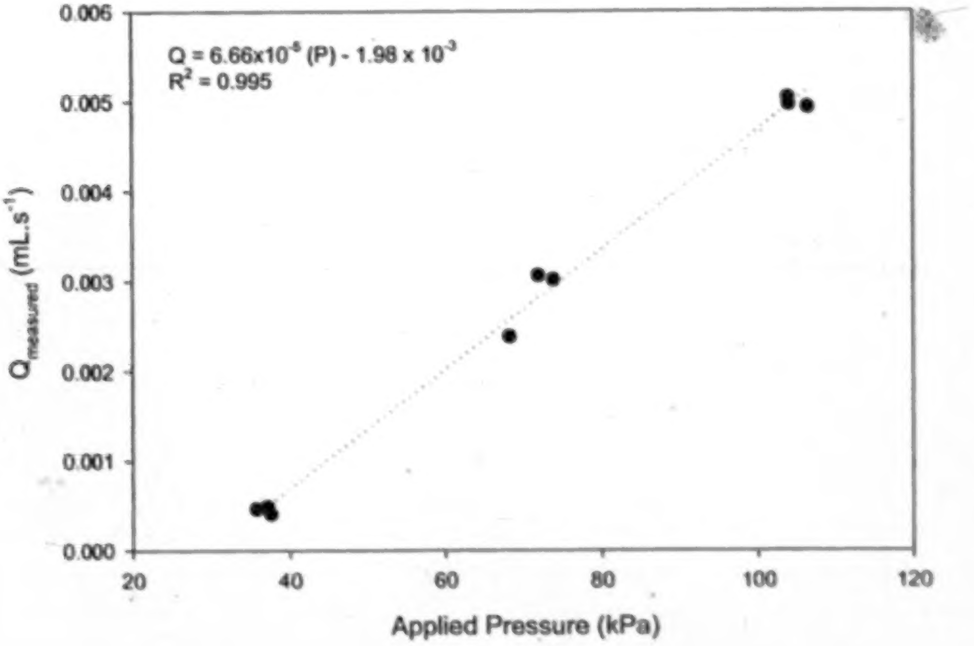

Figure 3.6 Measured diffusive air flow rates vs. applied pressure for membrane A.

As Figure 3.6 shows, diffusive air flow rate for an intact membrane is a linear function of applied pressure and may be presented for membrane A by the relationship shown in Equation 10:

$$Q_{diffusion} = 6.66 \times 10^{-5}P - 1.98 \times 10^{-3} \qquad [10]$$

where *P* is the applied (or test) pressure in kPa.

To determine the membrane parameter, κ, theoretical values of *N* (mol.m.s^{-1}) were calculated using the relationship, *N=DHPA*. These values were then converted to volumetric rates using the ideal gas law as given in Equation 11:

$$Q_{calculated} = \frac{NRT}{P} \qquad [11]$$

where, $Q_{calculated}$ is the theoretical volumetric flow rate of air (mL.m.s^{-1}), P is the atmospheric pressure (atm) (the downstream pressure), R is the universal gas constant (82.06 mL.atm.mol^{-1}.K^{-1}) and T is the absolute temperature (K). The value of κ (m^{-1}) was then estimated using the measured diffusive air flow rates ($Q_{measured}$, mL.s^{-1}) shown in Equation 12:

$$\kappa = \frac{Q_{measured}}{Q_{calculated}} \qquad [12]$$

Figure 3.7 presents the estimated values for κ as a function of applied pressure.

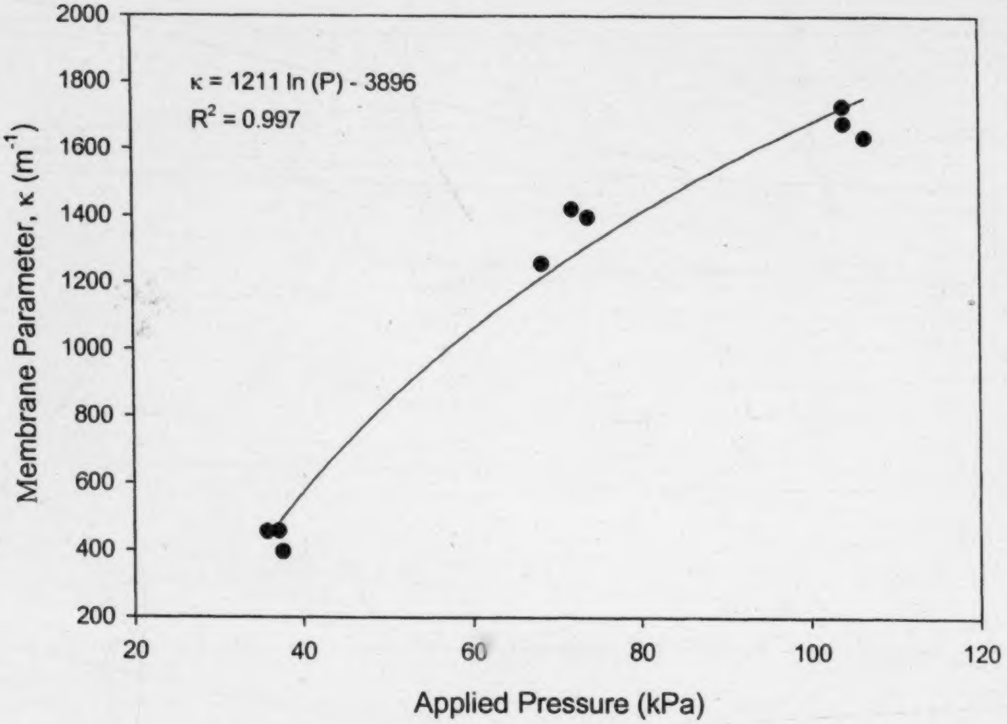

Figure 3.7 The membrane parameter (κ) for membrane A vs. applied pressure.

Figure 3.7 indicates that the membrane parameter (κ) for an intact ZeeWeed® 500 membrane may be estimated using the relationship given in Equation 13:

$$\kappa = 1211\ln(P) - 3896 \qquad [13]$$

where P is applied pressure in kPa. The variation of κ with applied pressure indicates that applied pressure may impact one or more of the parameters which are included in the term κ such as pore tortuosity, effective diffusion path and membrane porosity. At higher applied pressures, pore tortuosity may be reduced, resulting in higher diffusive flow than that estimated by Fick's law. In addition, as applied pressure is increased, the porosity of a polymeric membrane may also increase as the pores begin to expand. Higher applied pressures may also drive out some of the trapped water in the pores, resulting in a reduced length of diffusive path. One or a combination of these effects are expected to increase the rate of diffusive flow of an intact membrane over those estimated by equation Fick's first law of diffusion, without the term κ (Equation 3).

3.4.3. Model Verification

To verify the relationship for κ (Equation 13), diffusive air flow rates for an intact membrane, with a larger surface area (membrane B, surface area = 0.21 m^2) were measured at applied pressures between 35 to 103 kPa (5 to 15 psi) as described earlier. The integrity of membrane B was verified first, by determining its bubble point pressure as described in previous sections. Diffusive air flow rates for membrane B were also predicted by Equations 5 and 11 using κ values estimated by Equation 13. As Figure 3.8 indicates, the measured values for diffusive air flow rates seem to fit the predicted values.

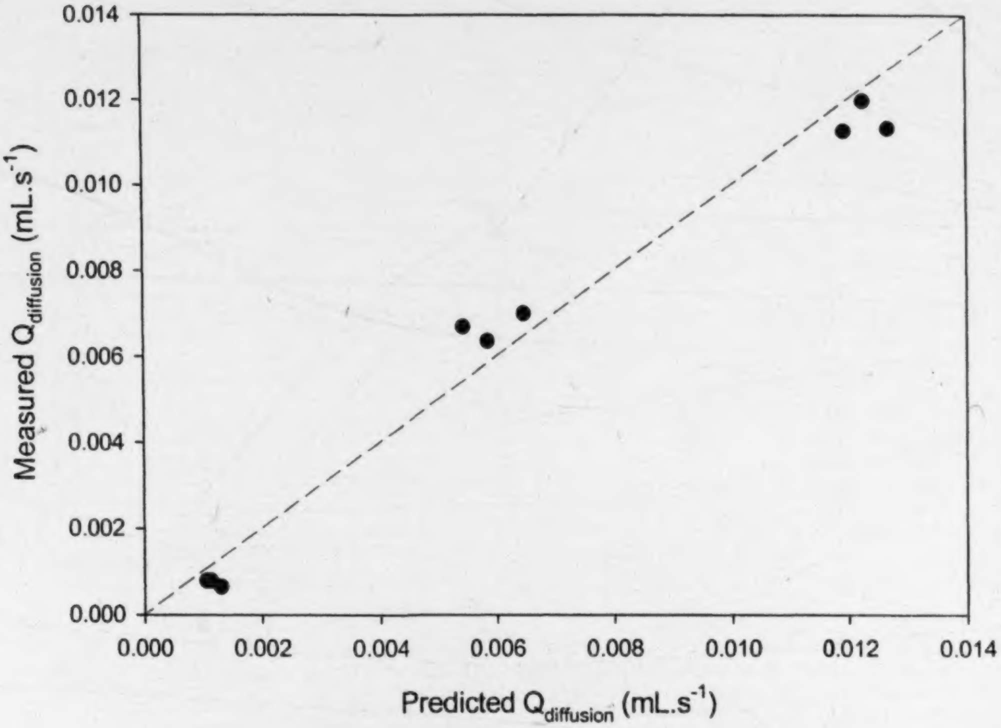

Figure 3.8 Predicted and measured diffusive air flow rates for membrane B.

These results indicate that the membrane parameter (κ) for a specific membrane is primarily a function of applied pressure and is independent of membrane surface area. Furthermore, κ can be used to closely predict air flow rates due to diffusion for intact ZeeWeed® 500 membranes with different surface areas.

3.4.4. Determination of Pressure Decay Rate due to Diffusion

Once the diffusive air flow rates have been determined for an intact membrane, pressure decay rates (PDR) resulted from such diffusive airflows can be readily predicted using Equation 9. The PDR for membrane B was estimated using the predicted diffusive air flow rates and were compared with the actual pressure decay rates which were measured during the experiments. Figure 3.9 shows the predicted PDR vs. the measured PDR for the intact membrane B at test pressures of 35, 69, and 103 kPa. As the results indicate, predicted PDR for the intact membrane were in close conformity with the measured values. The predicted values deviated slightly from the measured PDR at the test pressures of 69 and 103 kPa (10 and15 psi). At 69 kPa the predicted PDR was slightly lower than the measured PDR, indicating that this model underestimated the actual PDR. This indicates that the model prediction at 69 kPa (10 psi) would be somewhat conservative, which is desirable for regulatory purposes. At the applied pressure of 103 kPa (15 psi), the predicted PDR was higher than the measured PDR. This deviation may be, in part, attributed to the possible impact of applied pressure on the volume of lumens and consequently on the upstream volume (V) in Equation 9. It may be postulated that, at the applied pressure of 103 kPa, the hold-up volume would be larger than that estimated as the fibre inflates. A larger hold-up volume would yield predicted PDRs that are closer to those measured.

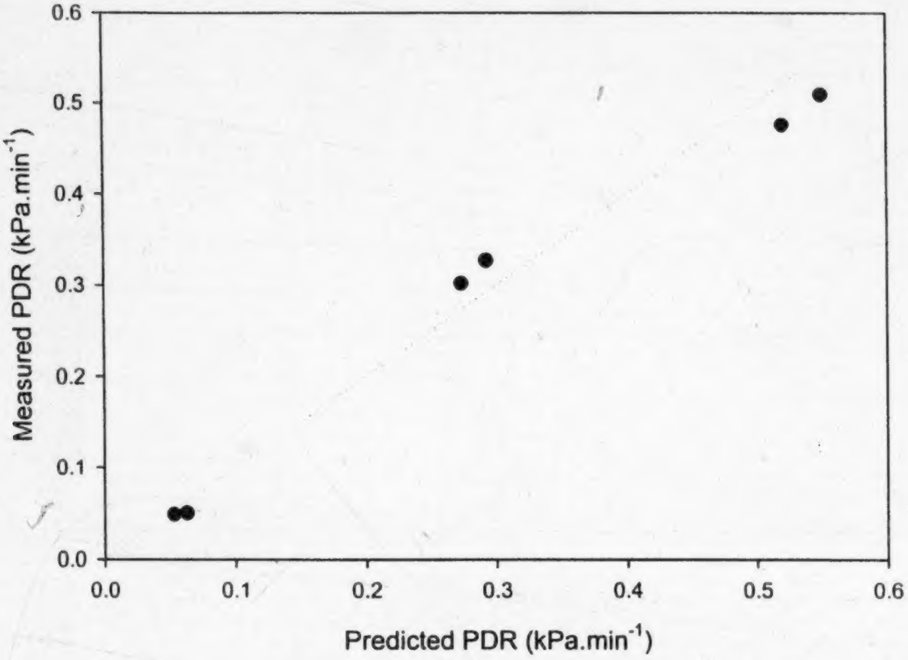

Figure 3.9 Predicted vs. measured PDR for an intact bench-scale membrane.

3.5. CONCLUSIONS

Results from the bench-sale determination of diffusive air flow rate through an intact bench-scale ZeeWeed®500 membrane provided the basis for estimating a membrane parameter (κ) for this membrane. This membrane parameter, which is specific to the ZeeWeed®500 membrane, accounts for the effect of pore tortuosity, effective diffusive path and porosity in the calculation of diffusive air flow rates through an intact membrane, using Fick's first law of diffusion. The membrane parameter, κ, was shown to be a function of applied pressure, indicating that the applied pressure may impact pore tortuosity, the effective length of diffusive path, and/or membrane porosity. Incorporating κ in the Fick's first law of diffusion allows for a relatively accurate estimation of diffusive air flow rates through intact ZeeWeed®500 membranes with various surface areas. Using the estimated diffusive flow rates, one can then determine the pressure decay rate for an intact membrane with an acceptable degree of accuracy. Knowledge of the pressure decay rates for an intact membrane enhances the pressure decay test in three different ways.

1. The estimated pressure decay rate provides a more accurate baseline for evaluating the integrity of a membrane using the pressure decay test.

2. Knowledge of the pressure decay due to diffusion for an intact membrane allows for a more realistic determination of theoretical log removal values, based on results from pressure decay tests.

3. Subtracting the expected pressure decay rate due to diffusion from the measured values improves the sensitivity of pressure decay tests and reduces errors associated with the dilution effect.

Further work is underway to determine the true effect of water temperature (especially low water temperatures) on the diffusive air flow rates. In addition, since pressure decay tests for immersed membranes may be performed while the membrane is fully submerged, future work will also evaluate the impact of submergence on the rate of air diffusion through an intact membrane. Further verification of Equation 12 in a pilot plant combined with challenge studies is also needed.

3.6. REFERENCES

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CHAPTER 4. IMPACT OF TEMPERATURE, SUBMERGENCE AND FOULING ON PRESSURE DECAY TEST FOR INTACT IMMERSED MEMBRANES*

4.1. INTRODUCTION

Recent concerns regarding the microbial quality of drinking water coupled with more stringent water quality requirements has given a new impetus to non-conventional water treatment technologies. This is primarily driven by the new regulations in the United States and Europe that require enhanced removal of pathogenic microorganisms while minimizing the formation of disinfection by-products. The Long-Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) requires additional treatment for those systems with elevated levels of *Cryptosporidium* spp. beyond conventional treatment. One of the alternate technologies that have been used extensively in the past decade is low-pressure membrane filtration; namely microfiltration (MF) and ultrafiltration (UF). MF and UF membranes have shown to be effective barriers against *Cryptosporidium* spp. and *Giardia* spp. and bacteria (Jacangelo et al. 1991; Adham and Jacangelo 1994; Freeman et al. 1996; Hirata and Hashimoto 1998; Karimi et al. 2002). The United States Environmental Protection Agency (USEPA) has proposed specific log removal credits for MF and UF membranes provided that the microbial removal efficiency of the membrane has been established through challenge studies and that the membrane systems undergoes periodic direct integrity monitoring testing (USEPA 2002).

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* A version of this Chapter will be submitted for publication to the Journal of Membrane Science.

Monitoring the integrity of low-pressure membranes has been the subject of extensive research in the past five years. The integrity monitoring tests are used in the membrane water treatment industry to detect the presence of an oversized pore or a defect that may result in the passage of pathogenic microorganisms. Most current integrity monitoring tests focus on detecting defects of the size that would hinder the effectiveness of MF and UF membranes in removing *Cryptosporidium* spp. Some of the existing integrity monitoring tests provide a direct indication of the presence of defects and are hence referred to as the direct integrity monitoring tests. The majority of these tests are based on the concept of the bubble point pressure and are conducted under certain applied positive or negative pressure. The bubble point test, the pressure decay or hold test, the vacuum decay test and the diffusive airflow test are among the most widely used direct integrity monitoring tests. Briefly, when the upstream side of a wetted membrane is pressurized with air or another test gas (i.e. nitrogen); gas tends to diffuse through the water filled pores of the membrane and exit at the downstream side of the membrane. As air pressure is increased, larger volumes of air are transferred to the downstream side. At a certain pressure, commonly referred to as the bubble point pressure, water vacates the largest pore(s) and air passes freely through the emptied pore(s) giving rise to the passage of larger volumes of air. The bubble point pressure can be related to the diameter of the largest pore or defect by Equation 1:

$$P = \frac{4 k \gamma Cos \ \theta}{d} \qquad [1]$$

where P is the bubble point pressure (Pa), k is the correction factor for the shape of the largest pore, γ is the surface tension of the wetting liquid in (N.m^{-1}), θ is the contact angle between the liquid and the membrane, and d is the diameter of the largest pore (m). A pressure decay or diffusive flow test is typically conducted at pressures below the bubble point pressure of an intact membrane. The upstream side of a wetted membrane is pressurized with air to a specific pressure and the pressure source is isolated. Lack of membrane integrity is signalled if the rate of pressure loss or air flow is above an acceptable value. Of the current direct integrity monitoring tests, the pressure decay test is the most widely used in the water treatment industry.

Farahbakhsh and Smith (2003) showed that loss of pressure during a pressure decay test for an intact membrane is primarily due to the diffusion of air through the wetted membrane pores. They proposed Equation 2 for predicting the rate of diffusion through an intact wetted ZeeWeed500$^{©}$ membrane:

$$N = \kappa DH \ (P_1 - P_0) A \qquad [2]$$

where,

N = the molar flow of diffused air, mol.s^{-1};

κ = The membrane parameter (ϵ/ξ L) (m^{-1}), representing pore's tortuosity (ξ), membrane porosity (ϵ), and effective length of diffusive path (L);

D = the diffusivity constant for air-water system ($m^2.s^{-1}$);

H = Henry's Law constant ($mol.atm^{-1}.m^{-3}$);

P_1 = the applied test pressure (atm);

P_0 = the downstream pressure (atm); and

$\bar{A}$ = membrane's surface area (m^2).

Several factors, however, may affect the rate of diffusion of air through membrane pores and hence the outcome of a pressure decay test. For an immersed membrane, these factors include the water temperature, the extent of membrane fouling, and the effect of submergence of the membrane during the test.

Water temperature affects its surface tension, wetting ability and as well the solubility and rate of diffusion of air through water. For example, the solubility of gases in water decreases with increasing water temperature while the diffusion rate of gases in water increases as water temperature increases. Temperature may also affect the characteristics of a polymeric membrane (κ in Equation 2) compounding the temperature effects on gas solubility and rate of diffusion. Little work has been conducted to evaluate the overall impact of water temperature on the pressure decay test, although the importance of such impact has been recognised by some investigators. For example, Hofman (1984) showed that a change in water temperature from 20°C to 5°C resulted in a 10% drop in diffusive flow rate of the test gas (nitrogen) during a diffusive air flow test of a flat-sheet membrane. Recently, Uhr

(2001) suggested that, for cold waters, the criteria for determining membrane integrity should shift to accommodate lower diffusion rates.

Membrane fouling on the other hand can result in restricted pores and overall reduced porosity and consequent reduction in the volume of air that diffuses through intact pores. Therefore, the consequence of membrane fouling is therefore expected be a drop in the pressure decay rates (PDR). The impact of membrane fouling on the pressure decay test has, for the most parts, been ignored and little published data is available with this respect. During a recent study (Hong et al. 2001) showed that membrane fouling had little to no effect on the sensitivity of pressure decay and diffusive airflow tests. This work, however, was conducted under pilot-scale and little data was presented to verify that conclusion.

For immersed membranes pressure decay tests are often conducted with the membrane submerged in water. Under such conditions, factors such as the degree of air saturation of the tank water may also impact the rate of air diffusion (N in Equation 2). In addition, under submerged conditions, the downstream pressure (P_0 in Equation 2) has to be determined and accounted for. It is, however, difficult to select a representative value for P_1, since submergence depth varies from 2.3 m at the bottom of the membrane to 0.3 m at the top of the ZeeWeed 500d© membrane. It is the determination of the representative downstream pressure that concerns this paper and not other impacts associated with conducting the pressure decay test under submerged conditions.

This paper, therefore, aims to determine the impact of water temperature, membrane fouling, and submergence on the results of pressure decay tests for the ZeeWeed500© membrane.

4.2. MATERIALS AND METHODS

A 0.21 m^2 hollow fibre membrane module was used throughout the experiments. The module was constructed at the University of Alberta laboratories using ZeeWeed500© fibres supplied by Zenon Environmental Inc. The membrane module was constructed as a 38 mm inside diameter pressurized unit. De-ionized (DI) water was used for all the test runs. The integrity of the membrane module was verified by determining its bubble point pressure. The method for determining the bubble point pressure has been described elsewhere (Farahbakhsh and Smith 2003).

4.2.1. Determining the impact of water temperature

To determine the effect of water temperature, the membrane module was placed horizontally in a water bath and the temperature was varied from 0 to 30°C using a heater and a refrigeration unit. The experimental setup is shown in Figure 4.1.

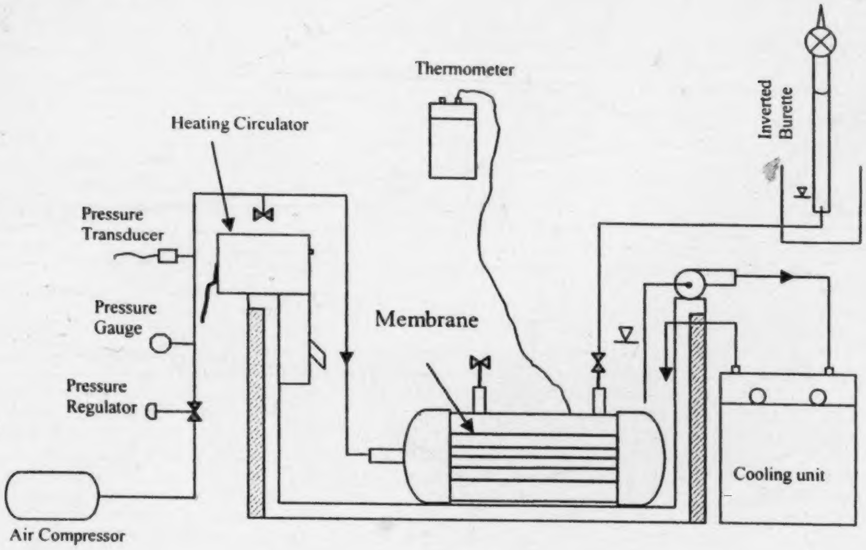
Thermometer
Heating Circulator
Inverted Burette
Pressure Transducer
Pressure Gauge
Pressure Regulator
Membrane
Cooling unit
Air Compressor

Figure 4.1 Experimental setup for determining the impact of water temperature on diffusive flow.

The membrane was wetted by filtering DI water in an outside-in configuration. The shell was filled with DI water and approximately 4L of DI water at the specified test temperature was filtered through the membrane using a Micropump© pump. The flux was maintained at 51 $Lm^{-2}h^{-1}$ (30 gfd) which is a typical flux for the ZeeWeed500© membrane. For each run, diffusive air flow rates were measured under isothermal conditions at 35, 70, and 103 kPa (5, 10, and 15 psi). For the zero degree runs, ice was added to the water bath. The shell was emptied and the lumens were pressurized from inside. When the desired pressure was reached, the membrane was isolated from the pressure source and both the pressure decay and diffusive air flow rates were measured. Diffusive air flow rates were measured by measuring the volume of air released in the shell using an inverted burette, as shown in Figure 4.1. Pressure decay rates were measured using a pressure transducer and a LabView© based data logging program.

4.2.2. Determining the impact of submergence

The experimental setup for determining the impact of submergence on the pressure decay test is depicted in Figure 4.2. Unlike the previous runs, once the membrane was sufficiently wetted, the shell was not drained. Instead, the drain line was connected to a riser tube (6 mm inside diameter polyethylene), the height of which was varied from 0.65m to 2.1m. When the lumens were pressurized under such conditions, the water inside the lumens was forced out of the pores displacing the water in the shell. Since the shell was already full of water, this water then filled the riser tube and the remainder was discharged into the burette. Once the desired test pressure was reached, the diffusive air flow rates were measured by measuring the displaced water using the burette. The pressure decay rates were determined similar to the previous run using a pressure transducer.

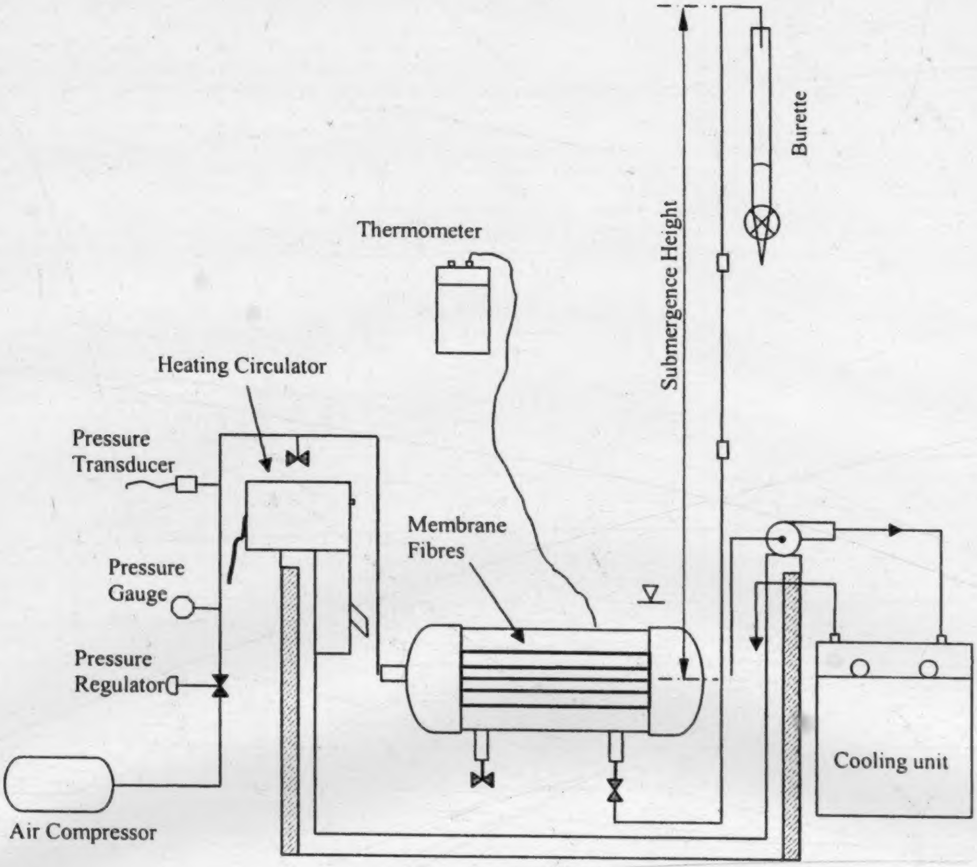
Burette
Submergence Height
Thermometer
Heating Circulator
Pressure Transducer
Membrane Fibres
Pressure Gauge
Pressure Regulator
Cooling unit
Air Compressor

Figure 4.2 Experimental setup for determining the impact of submergence on the pressure decay test.

4.2.3. Determining the impact of membrane fouling

Black tea was used to produce feed water high in natural organic matter (NOM). UV absorbance at 254 nm was used as a surrogate for quantifying the NOM content of the feed water. Feed water with three different NOM levels were prepared by placing tea bags (3, 6 and 12 tea bags) in a beaker with 3500 mL of DI water at 60 °C for 40 minutes. The membrane was fouled by filtering the feed water containing NOM. Both transmembrane pressure (TMP) and permeate flux were monitored during all runs and specific flux at 20°C was then used as a measure of the extent of membrane fouling. All runs were performed at room temperature. Once the membrane was fouled, the shell side was emptied and the permeate side was pressurized with compressed air to about 70 kPa. Diffusive air flow rates were then measured using an inverted burette as shown in Figure 4.1.

4.3. RESULTS AND DISCUSSION

4.3.1. Impact of water temperature

Diffusive air flow rates for an intact membrane under test pressures of 35, 70, and 103 kPa were measured while water bath temperature was maintained at the specified test temperature (from zero to 30°C). A minimum of three measurements were collected at each test pressure and temperature. Figure 4.3 depicts the fluctuations in the diffusive air flow rates at different test temperatures. In most cases an increase in water temperature resulted in an increase in diffusive air flow rates with two exceptions; 5 and 10°C at 35 kPa. This phenomenon is better shown in Figure 4.4 where the ratio of diffusive air flow rates (averaged values) at a specified temperature to those at 20°C are plotted for all three tests pressures. Therefore, it appears from these data, that aside from the abovementioned exceptions, a drop in water temperature resulted in a corresponding drop in diffusive air flow rates. The drop in diffusive air flow rates was most noticeable at 0°C, with about 42% drop in diffusive air flow rate as compared with the same test at 20°C. Results of the pressure decay rates were also quite similar measuring a PDR of 0.18 kPa/min at a test pressure of 70 kPa and water temperature of 0°C, as compared to a PDR of 0.32 kPa/min for a similar test at 20°C (a drop of about 44%).

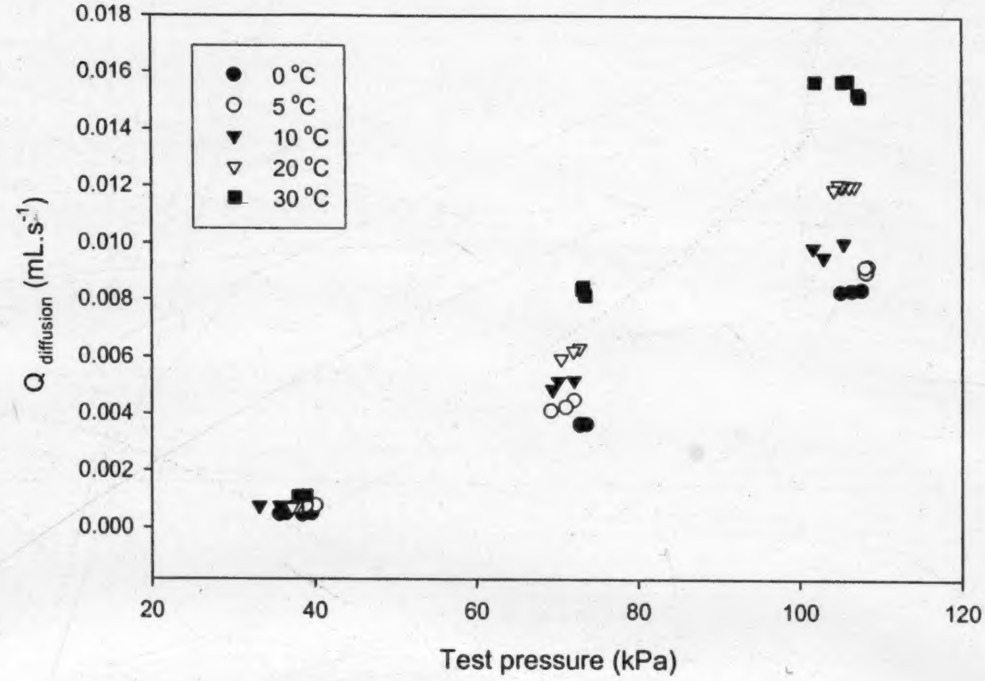

Figure 4.3 Diffusive air flow rates for the intact membrane at different water temperatures.

Variation in water temperature directly impacts Henry's constant (H) and the diffusivity (D) in Equation 2. Henry's constant will increase as water temperatures decrease, while diffusivity is expected to decrease with a drop in water temperature. The magnitude of drop in the diffusive air flow rate at very low water temperatures however, was higher than could be expected from the variation in D and H alone. This leads us to examine the impact of temperature on other properties of water such as surface tension, viscosity and contact angle, in addition to the properties of the membrane described by the parameter κ in Equation 2. Temperature affects both surface tension and density of water which, in turn, can impact rise of water in a capillary (capillary rise) according to Equation 3 (Zhmud et al. 2000):

$$h = \frac{2\gamma Cos\ \theta}{\rho g r} \tag{3}$$

where, h is the height of capillary rise (m), γ is the surface tension of the wetting liquid in

(N.m^{-1}), θ is the contact angle between the liquid and the surface of the capillary (in this case membrane pores), ρ is the density of water (kg/m^3), g is the acceleration of gravity (m/s^2) and r is the radius of the capillary (m). Both density (with the exception of the region between 4 and 0°C) and surface tension of water increase as temperatures drop. Temperature can also affect contact angle (θ) causing it to decrease with decreasing temperatures. The depth or height of water in the membrane pores (capillary rise), in turn, affects the rate of diffusion of air through a wetted membrane. Temperature can also impact the viscosity of water which, in turn, influences the rate of diffusion of air through the water column in membrane pores. The diffusivity constant (D) of gases in water has been shown to be inversely related to water viscosity using Equation 4 for oxygen (Wilke and Chang 1955):

$$D_{O_2-H_2O} = 7.4\times10^{-8}\frac{T\left(\psi_{H_2O}M_{H_2O}\right)^{\frac{1}{2}}}{\mu V_{O_2}^{0.6}} \tag{4}$$

where T is the absolute temperature (K), ψ_{H2O} is an association parameter for water, M_{H2O} is molecular weight of water (g/mol), μ is the viscosity of water (centipoises), and V_{O2} is the molar volume of oxygen (cm^3/g). Therefore, decreasing water temperature will result in further decrease in diffusivity of air constituents in water wetted pores.

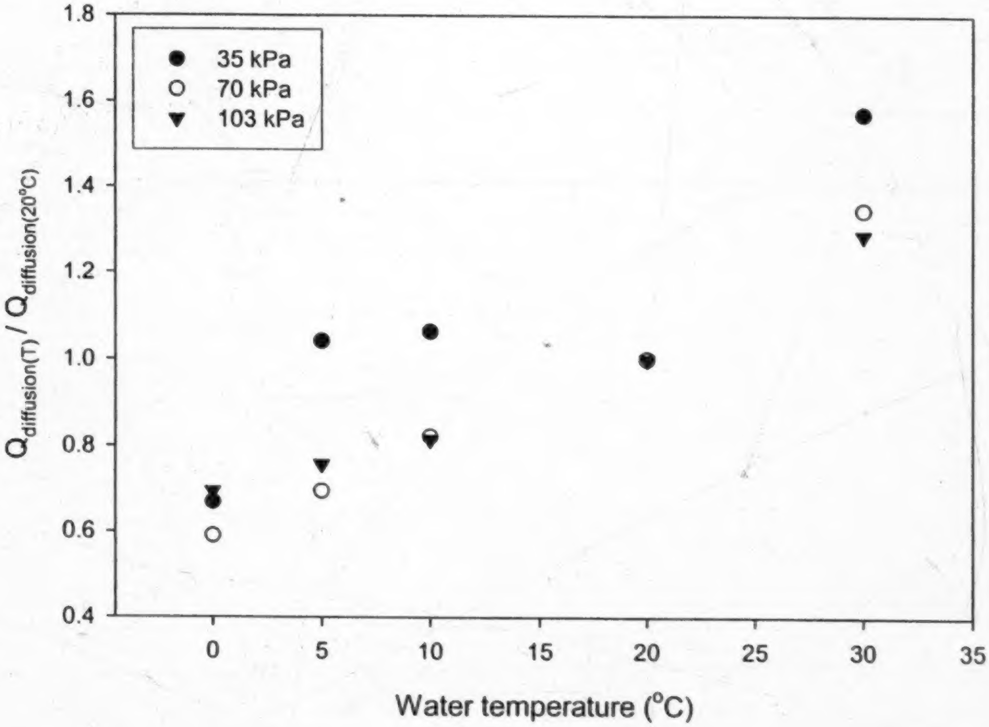

Figure 4.4 The ratio of diffusive air flow rates at different water temperatures and at 20°C.

The amount of water that can be forced out of capillaries (pores) of equal diameters is the function of a balance between the applied pressure and capillary and viscous forces in the membrane pores. As viscosity increases with the drop in temperature, so do the viscous forces and the amount of water that is forced out of membrane pores at a specific test pressure decreases, as a result of this. This will in turn decrease the rate of molar diffusion as the diffusive path would most likely be larger at lower temperatures.

Since the membrane in the study was a polymeric hollow-fibre membrane, a drop in water temperature most likely impacted the pore tortuosity and membrane porosity. Lower water temperatures, especially at 0°C, may have contracted the membrane resulting in lower porosity and higher degree of tortuosity and consequently lower κ. A smaller κ in Equation 2 means lower volumes of air diffusing through the wetted membrane. Therefore, a change in water temperature impacts the rate of diffusion of air through pores of a wetted membrane in a very complex manner, making it difficult to accurately predict such an impact using theoretical relationships and formulas. A similar phenomenon was observed by Hofman (1984) who found that the diffusion rate of nitrogen through a wetted flat-sheet membrane increased with increasing temperature up to 60°C, above which the rate of diffusion dropped. He attributed this phenomenon to the interaction between nitrogen solubility, diffusivity and water viscosity at higher temperatures.

A closer look at Figure 4.4 reveals that, although there are a couple of anomalies with data at 35 kPa, the data at 70 and 103 kPa appear to follow a very similar pattern. In fact, the ratio of diffusive flows at various temperatures for the 70 kPa and 103 kPa runs are close enough that they can be averaged and presented by the set of data shown in Figure 4.5.

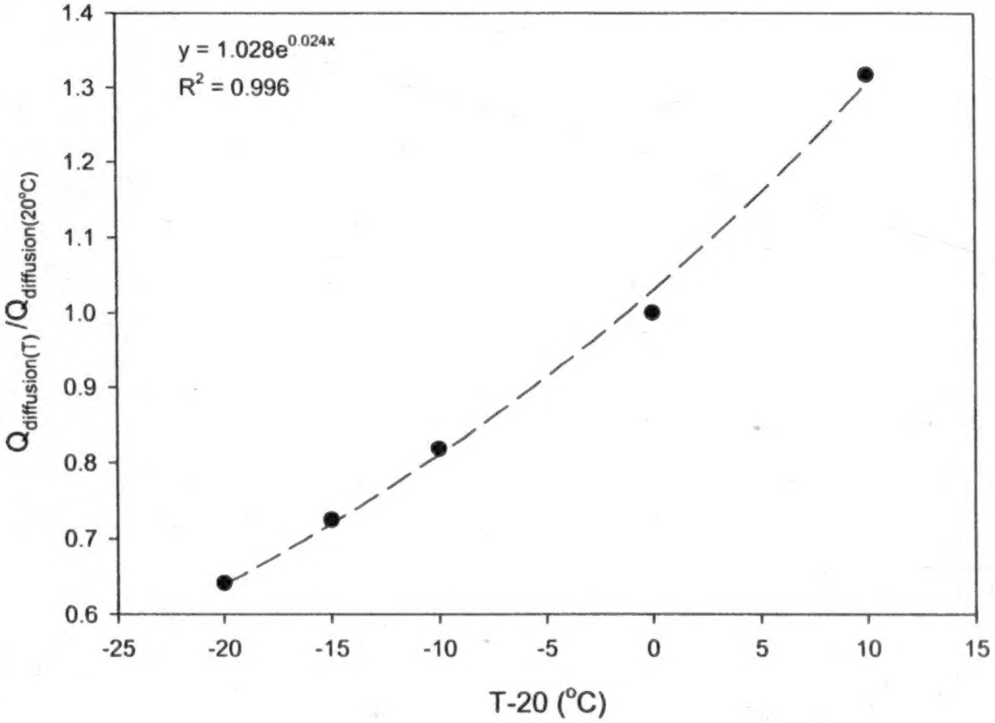

Figure 4.5 The averaged diffusive air flow rates ratios at 70 and 103 kPa vs. T-20°C.

The data shown in Figure 4.5 can be presented by the Equation 5 with a high goodness of fit ($R^2 = 0.996$).

$$Q_{diffusion\,(T)} = 1.028 Q_{diffusion\,(20^{\circ}C)} e^{0.024(T-20)} \qquad [5]$$

Equation 5, which follows an Arrhenius type relationship, can be readily used to predict the impact of temperature on diffusive airflow rates through an intact wetted membrane. Since Equation 5 was derived for only one type of membrane (ZW500d©), it should be considered unique for that membrane and may not be used in the present form for other polymeric membranes. This author, however, suspects that a similar relationship (with probably different constants) may be applicable to other polymeric membranes.

It would be interesting to determine the cause of anomalies observed at 5 and 10 °C for the test pressure of 35 kPa. It should be noted however, that data at 35 kPa are of little practical use to direct integrity monitoring tests as most manufacturers conduct such tests at pressures close to 70 kPa or higher.

It is interesting to note that a change in water temperature also impacts permeate flux, due primarily to change in water viscosity. This has been a well-known fact and several relationships are available to account for the effect of temperature on permeate flux. These relationships typically provide a correction factor for water viscosity. One such relationship was provided by Equation 6 and 7 (Karimi et al. 1999):

$$\text{(For T} \leq 20\,^{\circ}\text{C)} \quad \mu_T = e^{-0.0282(T-20)} \qquad [6]$$

$$\text{(For T} > 20\,^{\circ}\text{C)} \quad \mu_T = e^{-0.021(T-20)} \qquad [7]$$

where, μ_T is the viscosity of water at temperature T. Equations 6 and 7 are very similar to the correction term in Equation 5. Although the process of diffusion of air through wetted membrane pores is quite different than the flow of water through a membrane, both processes are affected similarly by temperature and it seems at the same rate. Although the similarity between Equations 5, 6, and 7 may be just a coincidence, it highlights the fact that of all parameters affected by temperature, the impact on water viscosity may ultimately be the most important consideration in determining the effect of temperature on diffusion of air through an intact wetted membrane.

4.3.2. Impact of submergence

As discussed earlier, the purpose of this study was also to determine the impact of submergence depth on diffusive air flow rates through an intact, immersed membrane. Many other factors aside from submergence depth may impact the diffusive air flow rates for a submerged membrane, including the degree of air saturation of water, water temperature, and degree of turbulence at the air-water interface near the membrane surface. The primary purpose of this study was to determine a representative downstream pressure (submergence depth) for an immersed membrane that was submerged from 0.3m to 2.3m. One approach was of course, to use an arithmetic average. This however, would only be representative if the variation of diffusive flow with depth was relatively linear. A non-linear relationship would indicate that another approach, perhaps a geometric mean, would be more suitable for determining a representative submergence depth or downstream pressure.

Figure 4.6 depicts the measured diffusive air flow rate values for an intact membrane submerged at 0.65m, 1.1m, and 2.1m. DI water at DO saturation levels of 80% to 85% were used for all the runs. All runs were conducted at test pressure of 70 kPa. Several interesting observations were made during the experiments. First, the diffusive air flow rates measured during the submergence runs were considerably lower than those measured with the empty shell, at the same test pressure. Lower diffusive air flow rates were somewhat expected, since, for the diffused air to displace water it must come out of solution which would not occur until the water in contact with the membrane surface is fully saturated. Therefore, at the beginning of the run, most of the diffused air dissolved in the water and did not contribute to the measured diffusive air flow rates. This phenomenon is partially responsible for the low diffusive air flow rates measured for all submerged runs. The second observation was that beyond the first two measurements, the diffusive air flow rates continued to increase the longer the test was carried out. This is also expected, since the increased saturation level of water within the shell allowed larger volumes of air to be released, displacing larger volumes of water and giving rise to higher measured diffusive air flow rates.

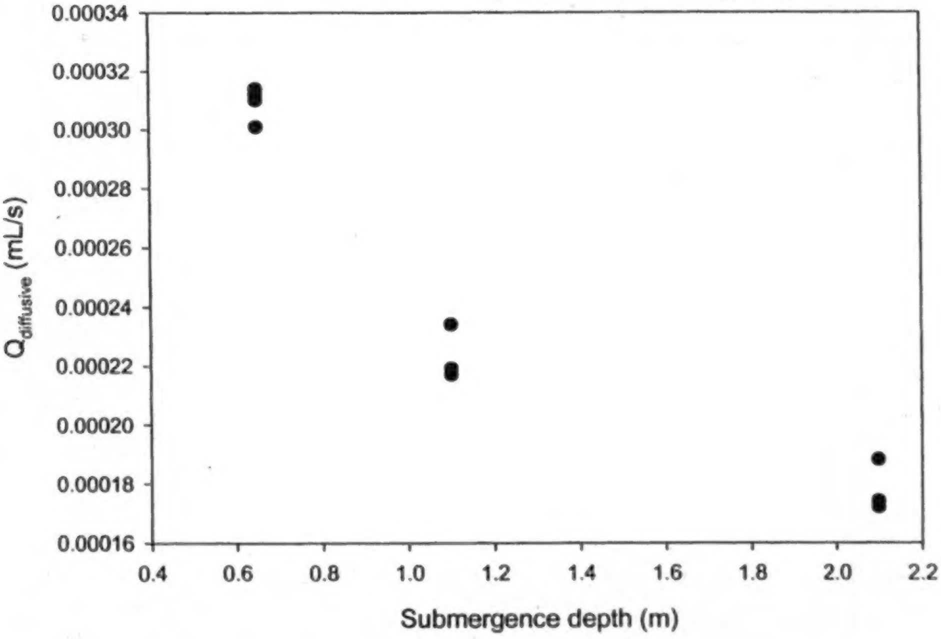

Figure 4.6 Diffusive air flow rates at different submergence depth for an intact membrane.

Although the results from the submerged trials are not representative of actual pressure decay or diffusive air flow tests, they provide sufficient evidence that an arithmetic mean of submergence depth may not provide an adequate representation of the downstream pressure during a pressure decay test. Based on the above results, it may be more prudent to use a geometric mean for determining the representative submergence depth and the downstream pressure.

4.3.3. Impact of membrane fouling

As indicated earlier, little work has been conducted to determine the impact of membrane fouling on the results from a pressure-driven integrity monitoring test.

Different fouling mechanisms such as pore plugging and the gel layer formation may reduce the loss of air due to diffusion during a pressure-driven integrity monitoring test. Figure 4.7 presents the results of diffusive air flow rate measurements for a clean and increasingly fouled intact membrane. The extent of membrane fouling is represented by the drop in specific flux corrected to 20°C. Each point in Figure 4.7 is the average of at least five different measurements. As the data in Figure 4.7 indicate, diffusive air flow rates for an intact membrane drop as the membrane is increasingly fouled. A similar trend was also measured with the pressure decay rates measured during the same trials, as depicted in Figure 4.8. Clearly, membrane fouling seems to reduce the rate of pressure decay for an intact membrane. This is somewhat expected since fouling either through pore plugging or gel-layer formation provides additional resistance to diffusion. In the case of pore plugging, the resulting reduction in overall porosity could lead to a reduced κ and consequent reduction in diffusive air flow rates as predicted by Equation 2. Reduction in the loss of air due to diffusion during a pressure decay test would consequently lead to a drop in pressure decay rates. Formation of a cake layer would not only reduce membrane porosity but also may increase the effective length of the diffusion path (L), further reducing both diffusive air flow rate and the pressure decay rate.

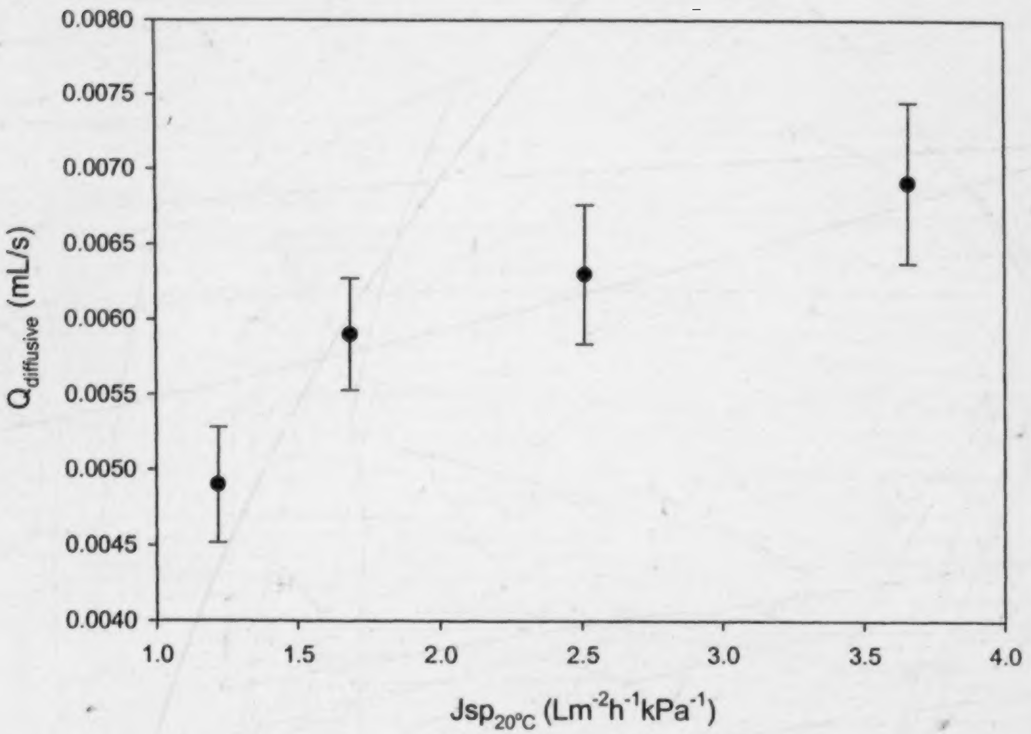

Figure 4.7 Diffusive air flow rates measured for an intact membrane with varying degree of fouling.

It is interesting that impact of membrane fouling on pressure decay rate has not been observed or reported under pilot or full-scale operating conditions. It is possible that the impact of membrane fouling on pressure decay or diffusive air flow rates is not measurable under large-scale operating conditions or such an impact may fall under normal measurement variations. It is, however, important to investigate this phenomenon in more detail under pilot or full-scale operations and determine if the impact is significant enough to demand modifications in interpreting the results of pressure-driven integrity tests, under varying operating conditions.

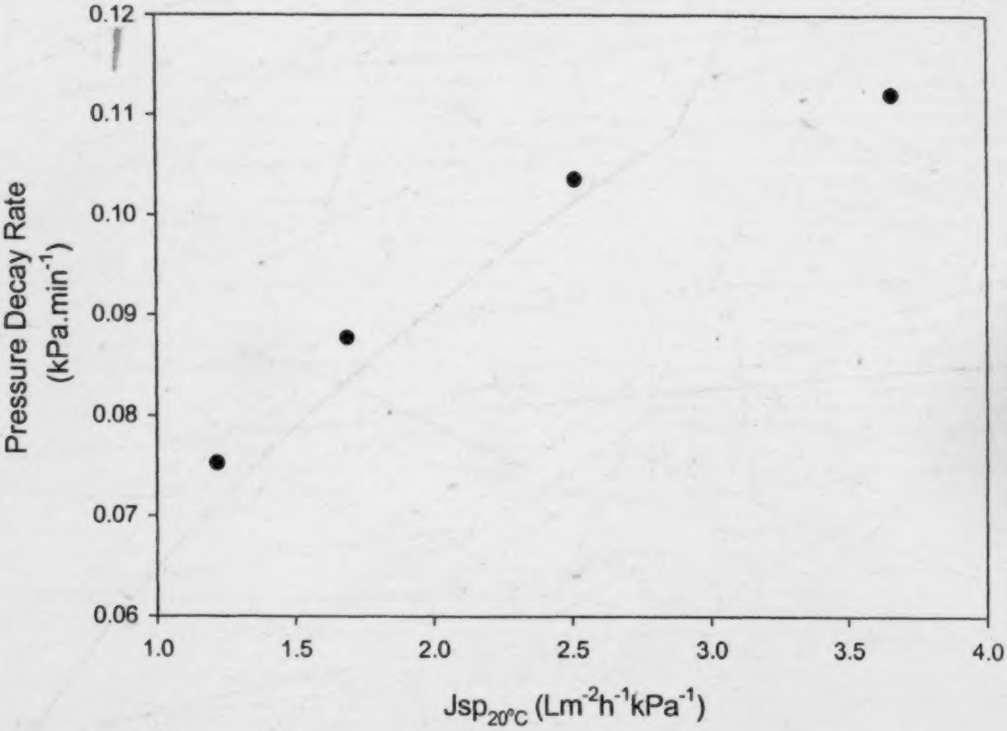

Figure 4.8 Pressure decay rates measured for an intact membrane with varying degree of fouling.

4.4. CONCLUSIONS

This work furthered the results of a previous study on estimating the contribution of diffusion to pressure decay for an intact membrane. It has been shown that among other factors, water temperature, submergence and membrane fouling impact the rate of air diffusion through an intact membrane. At the water temperature range of the tests (0°C to 30°C) diffusive air flows appear to be directly related to water temperature, decreasing with decreasing water temperature and vice versa. The drop in the rate of diffusion with temperature can be attributed to the effect of temperature on the properties of the wetting liquid (water in this case) such as viscosity, wetting ability (contact angle), density and surface tension. In addition, there seems to be further interactions between the temperature and polymeric membrane, resulting in perhaps lower porosity and increased tortuosity at very low water temperatures. One of the practical applications of this finding is the need to be cognizant of the effect of water temperature while conducting pressure-based membrane integrity tests, such as pressure decay tests and the diffusive air flow test. This is particularly the case with very low water temperatures as is experienced in northern Canada and the United States. The considerable drop in diffusive air flow rates and consequent decrease in pressure decay rate for an intact membrane as water temperatures approach zero, may mask the impact of a defect and should be accounted for. It appears that the criteria for membrane integrity tests in cold water should shift downward to account for the effect of temperature.

This study also showed that the submergence depth of an immersed membrane impacts the rate of diffusion in a non-linear fashion. To determine a representative depth and downstream pressure for use in Equation 2, a geometric mean would be more accurate than an arithmetic mean.

Finally, it was shown that the results of a pressure-based integrity test may be impacted by the extent of membrane fouling. As an intact membrane fouls more extensively, both the rate of air diffusion through wetted pores and the rate of pressure decay drop accordingly. Therefore, this preliminary work indicates that membrane fouling may mask the impact of a defect on pressure-based membrane integrity tests. There is, however, a need for further and more detailed investigation especially at the pilot and full-scale to verify this phenomenon and if possible, quantify the impact of membrane fouling on the results of pressure decay or diffusive air flow tests.

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CHAPTER 5. VALIDATION OF THE INTEGRITY OF TWO MEMBRANE PILOT PLANTS USING BACILLUS SPORE CHALLENGE TESTS[*]

5.1. INTRODUCTION

Recent outbreaks of waterborne illnesses coupled with consumer's demand for safer drinking water as well as improved detection techniques have led to increasingly stringent drinking water regulations. The Long Term 1 Enhanced Surface Water Treatment Rules (LT1ESWTR) and more recently the proposed Long Term 2 ESWTR (LT2ESWTR) require, in addition to reduced levels of disinfection by products, higher reduction in the level of pathogens such as *Cryptosporidium* spp. and *Giardia* spp. in the drinking water supplies. Due to their effectiveness in rejecting microbial pathogens such as *Cryptosporidium* spp., low-pressure membranes have emerged as the technology of choice for many water utilities. Intact microfiltration or ultrafiltration membranes have proven to be absolute barriers against *Cryptosporidium* spp. and are considered in the proposed LT2ESWTR as alternate technologies for further removal of these pathogens (USEPA 2001). The LT2ESWTR requires that microbial removal efficacy of low-pressure membranes that are proposed for water treatment be verified through conducting microbial challenge test with the microorganisms of concern or with suitable surrogate organisms. Bacterial spores, especially those of *Bacillus* spp., have been proposed as such surrogates and several microbial challenge studies involving these spores have been performed in the past (Hong et al. 2001; Trimboli 2001; Côté 2003). Of the many strains of *Bacillus*, *Bacillus subtilis* and *Bacillus megaterium* spores have emerged as most suitable candidates for conducting challenge studies. These spores are typically ellipsoid in shape, smaller than *Cryptosporidium* spp. with a diameter of about 0.5μm and a length of about 1.5μm. Due to their size they can be considered conservative surrogates for such pathogens as *Cryptosporidium* spp. (2 to 5μm) and *Giardia* spp. (5 to 15μm).

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[*] A version of this Chapter will be submitted for publication to the Journal of Water Supply.

While intact MF and UF membranes are absolute barriers against many pathogenic organisms of interest, the same cannot be said about a compromised membrane. MF and UF membranes with defects, oversized pores, or broken fibres can no longer serve as effective barriers against pathogenic microorganisms. As such, the LT2ESWTR requires all membrane water treatment plants to conduct regular direct integrity monitoring tests to verify microbial log removal values (LRV) for a specific membrane. These direct integrity monitoring tests provide instantaneous information about the presence of leaks, defects or broken fibres. Currently, the most widely used direct integrity test is the pressure decay test that relies on determination of loss of pressure resulting from leakage of air or another test gas through oversized pores or defects in a wetted membrane. Theoretical relationships are available that predict LRV of a membrane based on results from direct integrity monitoring tests. A detailed review of integrity monitoring tests for low-pressure membranes has been presented elsewhere (Farahbakhsh et al. 2003).

This paper presents the results of a challenge study conducted on two immersed low-pressure membrane pilot plants using *Bacillus megaterium* spores. The reliability of available theoretical models for relating direct integrity monitoring results to microbial LRV is also evaluated.

5.2. BACKGROUND

As indicated earlier, several models have been developed that predict the microbial LRV for low-pressure membranes based on results from direct integrity monitoring tests. One such model by Johnson (1998) predicts log removal of particles (including microorganisms) greater than $0.2\mu m$. The model assumes that all particles ($>0.2\mu m$) are rejected completely by an intact microfilter and that the portion of flow that passes through a defective fibre has the same concentration as that of the feed. The model relates the log removal values (LRV) of a microfilter (pore diameter of $0.2\mu m$) to results of pressure decay and diffusive airflow (DAF) tests as noted in Equation 1 and 2 (Hong et al. 1998):

$$LRV = \log\left[\frac{Q_{filt} P_{atm}}{V_{filt}} \frac{\mu_{water}(P_{test}^2 - P_{atm}^2)}{2\mu_{air} P_{filt} P_{atm}} \left(\frac{t}{\Delta P}\right)\right] \qquad [1]$$

$$LRV = \log\left[\frac{Q_{filt}}{Q_{DAF}} \frac{\mu_{water}(P_{test}^2 - P_{atm}^2)}{2\mu_{air} P_{filt} P_{atm}}\right] \qquad [2]$$

where, Q_{filt} is filtrate flow rate (L/min), Q_{DAF} is air flow rate from DAF test result (L/h), μ_{water}, μ_{air} are viscosity of water and air respectively (kg/m.s), P_{test}, P_{filt}, and P_{atm} are test air pressure, transmembrane pressure and atmospheric pressure (kPa), respectively, V_{filt} is filtrate pipework volume and $\Delta P/t$ is pressure decay rate (kPa/min). In a more recent work, (Hong et al. 2001) attempted to establish correlations between microbial removal efficiency of a pilot-scale microfilter and results of direct integrity monitoring tests (pressure decay and diffusive airflow tests). *Cryptosporidium spp*. oocysts, *E. coli* (ATCC 25922), and *Bacillus subtilis* spores were used for microbial challenge tests. Both direct integrity monitoring tests proved to be quite sensitive in detecting even one broken fibre. However, neither of the integrity monitoring techniques showed a statistically reliable correlation with microbial removal efficiency of the microfiltration system.

Spores of *Bacillus subtilis* and *Bacillus megaterium* have been used as surrogates to *Cryptosporidium* spp. oocysts during microbial challenge studies with low-pressure membranes (Trimboli et al, 2001; Côté et al, 2003). Using *Bacillus megaterium* spores in a 36 ML/d (9.5 mgd) water treatment plant, Trimboli and coworkers were able to verify greater than 5.9 log removal for a full-scale, microfiltration plant. Their results indicated that, under most conditions, the theoretical LRV calculations (Equations 1 and 2) provided a conservative estimate of log removal capability of the microfiltration membrane. Their work also demonstrated that due to substantial logistics of conducting spore challenge studies, spore challenge tests may not be a practical method for routine monitoring of membrane integrity. Côté et al (2003) challenged a pilot-scale immersed membrane with *Bacillus subtilis* spores and measured greater than 7 log removals by the intact membrane. The authors also showed that a theoretical relationship similar to Equation 1 produced conservative estimates of LRV for both an intact and a compromised membrane. Correcting for pressure decay rate (PDR), as shown in Equation 3, resulted in more accurate estimates of LRV for the immersed membrane.

$$\mathrm{PDR}_{\mathrm{corrected}} = \mathrm{PDR}_{\mathrm{measured}} - \mathrm{PDR}_{\mathrm{Diffusion}} \qquad [3]$$

where, $\mathrm{PDR}_{\mathrm{diffusion}}$ is the pressure decay rate for an intact membrane resulting only from diffusion.

In another study, (Farahbakhsh and Smith 2003) developed a model, based on the Fick's first law of diffusion, to estimate the contribution of diffusion to pressure decay test for the ZW500© hollow fibre membrane. The model which is presented in Equation 4, could predict the rate of air diffusion through an intact wetted membrane for pressure ranges between 35 and 103 kPa (5 to 15 psi), with relative accuracy. The authors also showed for an intact membrane, pressure decay is entirely attributed to air diffusion through wetted pores.

$$N = \kappa DH(P_1 - P_0)A \qquad [4]$$

where, N is the molar flow of diffused air, mol.s^{-1}, D is the diffusivity constant for air-water system, m^{2}.s^{-1}, H is Henry's Law constant for the gas used, air in this case (mol.atm^{-1}.m^{-3}), P_1 and P_0 are the applied pressure and the downstream pressure (atm) respectively, and A is the membrane's surface area, m^{2}. In Equation 4, κ is the membrane parameter (m^{-1}) and must be determined experimentally, since it describes the membrane's specific properties such as pore tortuosity, porosity and effective diffusion length.

The proposed Long Term 2 ESWTR (LT2ESWTR) places a major emphasis on alternative treatment technologies including UF and MF membranes. According to the proposed LT2ESWTR, a membrane process can receive *Cryptosporidium* spp. removal credits by either demonstrating its removal efficiency through challenges testing or by determining a maximum log removal value based on the results of a direct integrity monitoring test (USEPA 2001). The proposed rule provides brief guidelines for conducting challenge testing and sets performance criteria for direct integrity monitoring tests. The upcoming guidance manual for membrane filtration (which is being prepared by the USEPA) will provide more detailed guidelines for challenge testing of membrane filters (Allgeier 2003).

In terms of challenge testing, the rule allows the use of either *Cryptosporidium* spp. oocysts or an appropriate surrogate which can be shown to be removed more efficiently than *Cryptosporidium* spp. oocysts. The challenge testing can be performed on a full-scale or a smaller scale module, if challenge results and integrity test results are scalable to full-scale performance.

The proposed LT2ESWTR establishes three criteria for direct membrane integrity tests; resolution, sensitivity, and frequency. Resolution has been defined as the ability of the direct integrity test to detect breaches of membrane integrity in the order of 3-μm or less (within the size of *Cryptosporidium* spp.). The sensitivity criterion on the other hand requires that the integrity test be able to verify, as a minimum, the log removal credits that have been awarded to the membrane system. The proposed rule defines sensitivity, in terms of verifiable log removal, by Equation 5:

$$LRV_{Max} = LOG\left[\frac{Q_{Filtrate}}{CF \times Q_{Breach}}\right] \qquad [5]$$

where LRV_{Max} is the maximum log removal value that can be verified by a direct integrity test, $Q_{Filtrate}$ is the total design permeate flow from the membrane unit, Q_{Breach} is the total flow from the smallest breach that the direct integrity test can detect, and *CF* is the concentration factor. Concentration factor must be defined for each membrane system (i.e. membrane type and configuration) and is a measure of increase in the concentration of contaminants in contact with the membrane relative to the feed water. The actual magnitude of the CF may vary from 1 to 20 for different membrane systems.

The following sections discuss the procedure for conducting microbial challenge testing of two immersed hollow fibre membrane pilot plants with bacterial spores and present the results of the challenge tests. This study was conducted in the light of the proposed LT2ESWTR and its requirements for direct membrane integrity tests to meet the criteria of sensitivity.

5.3. MATERIALS AND METHODS

All spore challenge studies were conducted at the pilot facilities of Zenon Environmental Inc. in Burlington, Ontario. Two different ZeeWeed© pilot plants were used during the study; ZW500d© and ZW1000a©. Pilot plant specifications are summarized in Table 5.1.

Table 5.1 Summary characteristics of the two membrane pilot plants used during the challenge tests.

	ZW500d©	**ZW1000©**
No. of modules	3	3
Module's Surface area	31.6 m^2 (340 ft^2)	37.2 m^2 (400 ft^2)
Total surface area	94.8 m^2 (1020 ft^2)	111.5 m^2 (1200 ft^2)
Pore size	0.04 to 0.1 μm	0.02 to 0.1 μm
Inside/outside diameter	0.75 mm/1.95 mm	0.35 mm/0.65 mm
Flux	50 Lmh (30 gfd)	50 Lmh (30 gfd)
Available tank volume	880L	210L
Operation mode	Dead end	Dead end
Recovery	100%	100%
Mixing mode	aeration	Permeate recirculation
Feed	Stored permeate	Stored permeate
Backpulse Flux	50 Lmh (30 gfd)	50 Lmh (30 gfd)
Backpulse Duration	15 seconds	15 seconds
PDT Pressure	62 kPa (9 psig)	69 kPa (10 psig)
PDT Duration*	5 minutes	5 minutes
* PDT = Pressure decay test		

As is indicated in Table 5.1, one of the main differences between the ZW500d© and the ZW1000© membranes is the inside diameter of their fibres. The relatively new ZW1000© membrane has fibres with an inside diameter of 0.35 mm, less than half of the inside diameter of the ZW500d© fibres. Another difference between the two units is that the ZW1000© fibres are not supported while theZW500d© fibres are, and hence their outside diameter is almost three times larger than the ZW1000© fibres. According to the Zenon Environmental, both fibres are manufactured from the same polymer, although the method of manufacturing is different. In addition, the ZW1000© fibres have a slightly smaller pore size distribution than the fibres from the ZW500d© membrane.

Both pilot units were fully automated and the transmembrane pressure (TMP), permeate flow and flux, and feed water temperature were continuously monitored throughout the study. For each pilot study, the *B. megaterium* spore suspension was diluted with permeate to a desired concentration and the diluted spore suspension was pumped to the feed line of the membrane using a Masterflex peristaltic pump.

The challenge tests were performed on intact, as well as compromised membranes. Membranes fibres were increasingly compromised with one and two pinholes, followed by one and two cut fibres. Pinholes were introduced using a hypodermic needle. Care was taken to ensure that the pinhole was introduced only on one side of the fibre. The second pinhole was introduced on the same fibre but at a different location. Fibres were cut using sharp scissors. Care was exercised to ensure that the fibre's tip was not pinched during the cut. All fibres were cut close to the permeation point to simulate the worst-case scenario. To make the best use of the available spores, the content of the ZW1000© tank was stored in a separate 1000L polyethylene tank which was later on used as the starting feed for the ZW500d© pilot. In total, about 400L of feed water with high spore counts was pumped to the ZW500d© tank prior to the start of the challenge test for this unit. Once the first challenge test was completed for the ZW500d© unit, the content of the tank was stored in the 1000L tank for the second challenge test. In this way, it was ensured that the starting tank concentration of *Bacillus* spp. spores for subsequent challenge test was maximized.

Pressure decay tests (PDT) were performed before feeding spores for the intact and compromised membrane. A minimum of two PDT were performed for each scenario. Pressure decay tests were conducted manually using a digital pressure gauge, a pressure regulator and pressurized air at 62 and 69 kPa (9 and 10 psi) for the ZW500d© and ZW1000©, respectively. The PDTs were performed while the membranes were submerged. The dissolved oxygen levels of the tank water, as well as water temperature, were measured and recorded at the start and completion of the PDT. Water samples were collected from the permeate, feed and membrane tank at specific intervals. At least three sets of samples were collected for each challenge test condition (i.e. intact membrane, 1 pinhole, 2 pinholes, etc.).

5.3.1. Spore Production

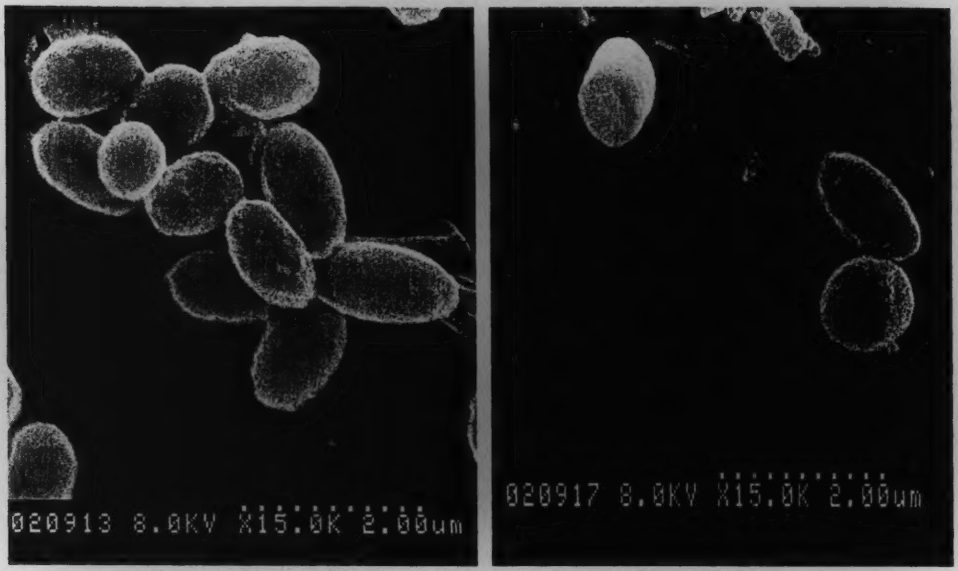
Two strains of *Bacillus* spp. bacteria were investigated for sporulation; *Bacillus subtilis* (ATCC 19659) and *Bacillus megaterium* (ATCC 14581). Both strains are non-pathogenic and have been used extensively in sporulation research. A modified Shaeffer media, 8 g/L nutrient broth, 0.25 g/L $MgSO_4.7H_2O$, 1 g/L KCl, 1 μM $FeSO_4$, 10 μM MnCl, and 1 mM $CaCl_2$ was used for all sporulation work.

The pH of the media was raised to 8.0 with NaOH prior to inoculation. Growth and sporulation of *Bacillus* spp. was performed in a 50L fermenter at 37°C with 40 L/min of aeration. Sporulation was usually complete within 60 to 72 hours, although sporulation periods in excess of six days were also encountered. The suspension was filtered using a cross flow plate-and-frame membrane to reduce its volumes to10 L. Pellets were then formed by centrifuging the concentrated suspension in 1-L containers at 7500 RCF for 20 minutes. The supernatant was withdrawn and the pellets were resuspended with sterile deionized (DI) water and were centrifuged again. The process was repeated until the supernatant was clear. The pellets were resuspended again and heat-treated in a water bath at 80°C for 15 minutes. The spore suspension was centrifuged again and the final pellets were resuspended in a 50% ethanol solution and refrigerated for long-term storage. The overall yield for each sporulation run was approximately 4×10^{12} total spores. In total, approximately 2×10^{13} spores were produced over an eight-week period for the challenge tests. Plate 5.1 shows scanning electron microscopy (SEM) images of *Bacillus subtilis* and *Bacillus megaterium* spores. The measurements of the SEM images revealed that spores from both strains have ellipsoid shapes and are approximately of the same size (*B. subtilis* spores are 0.7 μm × 1.4 μm and *B. megaterium* spores are 0.8 μm × 1.4 μm). *Bacillus megaterium* showed much higher spore production rate and typically sporulated faster than *Bacillus subtilis*. Therefore, it was decided to use the spores of *B. megaterium* for the challenge study. Several factors that appear to influence spore production rate included type of media, age of the starting culture (best results were achieved with a bacteria culture in log-phase growth), and aeration (higher aeration rates resulted in faster and more complete sporulation).

5.3.2. Spore Enumeration

All samples were enumerated for spores at the laboratories of the University of Alberta.

Two methods were used for spore enumeration. Samples with expected high spore counts were enumerated using the pour plate method. Feed and tank samples were serially diluted and at least two dilutions were plated for each sample in triplicate. Permeate samples were enumerated using a combination of membrane filtration method and pour plate method. Only samples of permeate from the intact membrane runs were enumerated using the filtration method. A 100mL volume of permeate samples was filtered using 0.45 μm sterile membrane filters and a vacuum filtration apparatus. Each filter was then washed with 200 mL of sterile DI water and filters were placed in a 47 mm Petri plate containing nutrient agar. For compromised membranes, 1 to 4 mL of sample was enumerated by the pour plate method. All plates from both enumeration methods were incubated inverted at 37°C. Pour plates were enumerated daily for 6 days, while membrane filter samples were counted daily for 4 days, to ensure all spores were detected. All results were reported in CFU/100 mL of sample.



(a) (b)

Plate 5.1 SEM images of (a) *Bacillus megaterium* and (b) *Bacillus subtilis* spores.

During the enumeration of feed samples, it was discovered that the samples also contained relatively heat resistant bacteria or possibly fungal spores. These contaminants appear to withstand heat treatment at 80°C for 10 for 15 minutes. It was suspected that wastewater research conducted in the vicinity of the membranes used for challenge study may have contributed to the presence of these contaminants in the samples. To eliminate these contaminants, it was decided to reheat the samples to 100°C in a liquid cycle of an autoclave unit. Depending on sample volumes (10 mL dilutions or 300 mL permeate samples) the reheating was conducted for between 30 to 60 minutes. Heating the samples at 100°C for 30 to 60 minutes did not affect the spore counts (data not shown). All other contaminants were entirely eliminated from samples by reheating at 100°C.

Spore counting for the pour-plate method was carried out over a six-day period. Spore counts on the plates increased from day to day, reaching near maximum on the fourth day. Spore counting for the filtration technique was completed over a four day period, with two counts; one after the first 24 hours and the second on the fourth day. It took over one month to enumerate about 200 samples. All samples were enumerated in triplicate.

5.4. RESULTS AND DISCUSSION

Results of the challenge study are presented in terms of fluctuations in the LRV of *Bacillus* spp. spores as a function of the type of defect (i.e. 1 pinhole, 1 cut fibre, etc.), as well as the pressure decay rates in kPa/min, for each pilot unit. Figures 5.1 and 5.2 show how the extent of defect impacts the ability of each membrane pilot unit to remove the challenge microorganisms (*Bacillus* spp. spores). Both membranes, when intact, completely removed the spores of *Bacillus megaterium*. Six of the permeate samples from the intact membranes showed single colonies which were not of the *Bacillus* spp. strain. *Bacillus* spp. colonies were detected in four permeate samples from the intact membranes during the second challenge tests. This, however, was attributed to the background contamination from the previous challenge test, as permeate samples collected before spore addition also showed the presence of *Bacillus* spp. spores. Log removal values of greater than 7.0 were measured for both intact membranes. The LRV for the intact membranes was only limited to the concentration of spores in the feed or the tank water and higher LRV would have, most likely, been measured with a higher concentration of spores. For both membranes, a relatively sharp drop in the LRV was measured with the introduction of a pinhole (the pinhole size varied for each test) in one fibre, as shown in Figures 5.1 and 5.2. The steeper drop in the LRV for ZW1000© with one pinhole was most likely due to the size of the pinhole, as the PDR for the ZW1000© with a pinhole were about 1.8 and 4.26 kPa/min, as compared with 0.38 and 0.95 kPa/min for the ZW500d©. Addition of another pinhole on the same fibre did not appear to affect the LRV in a statistically significant manner, although the PDR was approximately doubled for the ZW500d© with the introduction of the second pinhole.

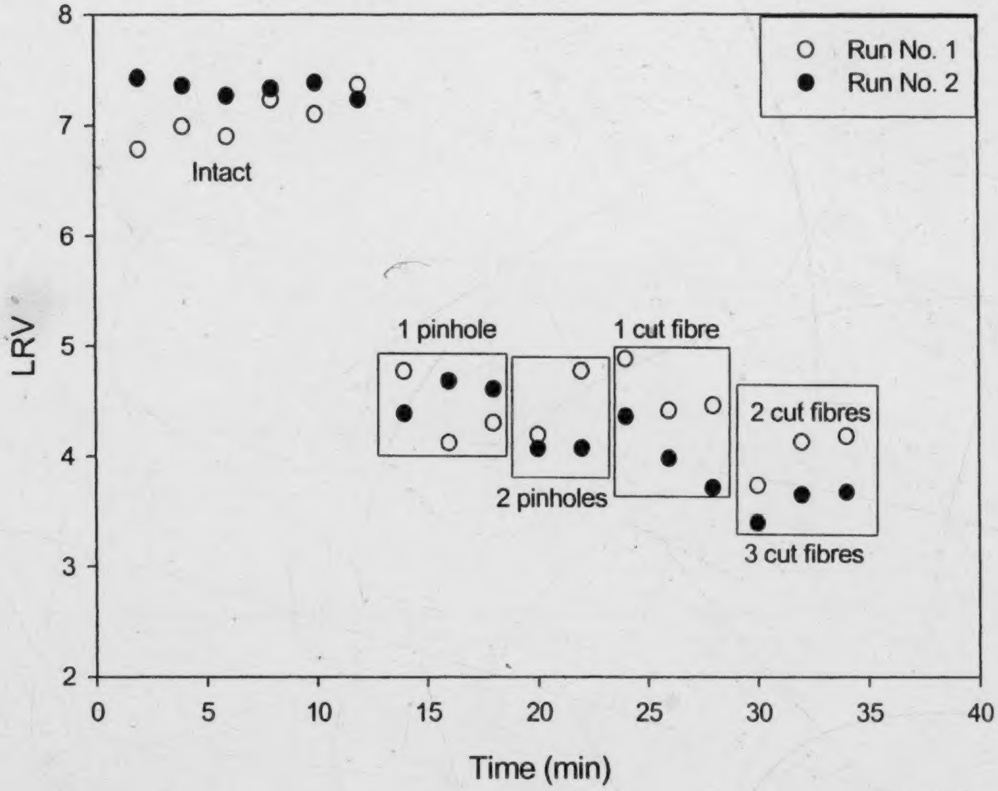


Figure 5.1 Impact of defects on LRV of *Bacillus* spores for the ZW1000© pilot.

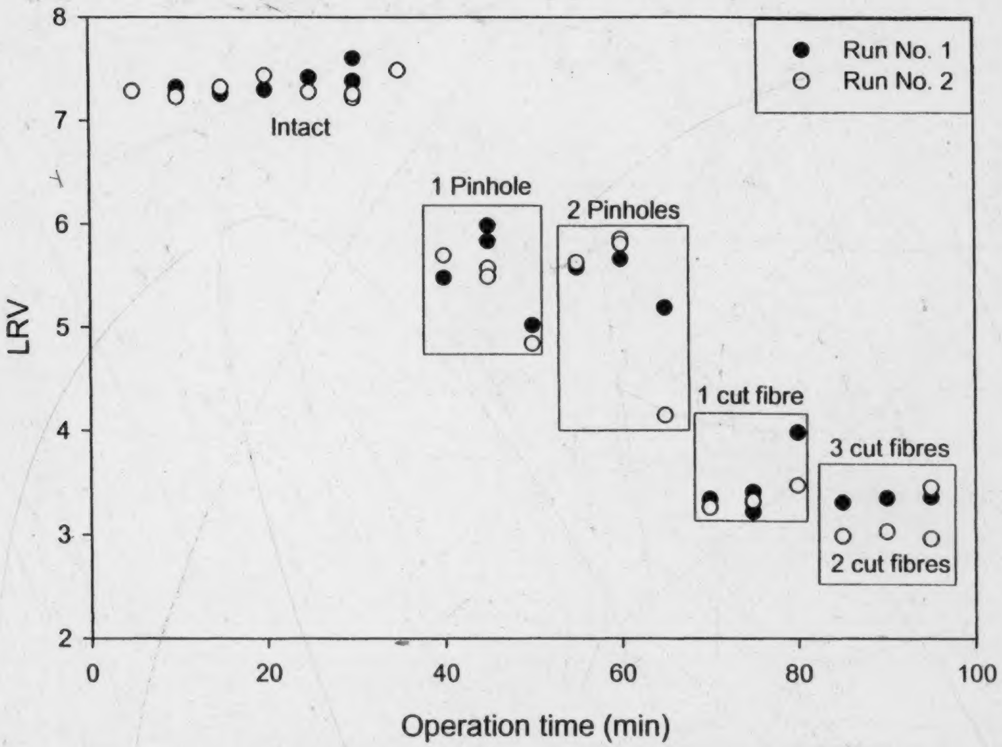


Figure 5.2 Impact of defects on LRV of *Bacillus* spores for the ZW500d© pilot.

The difference between the ZW1000© and the ZW500d© membranes became evident with the cutting of the first fibre. Although the removal efficiency of the ZW1000© dropped slightly as the result of the broken fibre, it was considerably higher (by over one log) than that of the ZW500d© under similar circumstances. This can be mainly attributed to the difference in the fibres' inside diameter. The broken ZW500d© fibre, with over two times the diameter, allowed the passage of larger volumes of water containing *Bacillus* spp. spores than the broken ZW1000© fibre. As shown in Figures 5.1 and 5.2, the difference in the LRV for one cut fibre versus two or three cut fibres, although statistically significant for the ZW1000© membrane, was not considerable. Both membranes were able to sustain close to 3 log removal of *Bacillus* spp. spores, even with three cut fibres.

A more practical method of representing the extent of the breach of membrane integrity is by expressing the number of compromised fibres as the percentage of the total number of fibres in the plant. For example, three compromised fibres for the ZW1000© pilot plant represents 0.003% of the total number of fibres in the unit. Similarly, for a ZW500d© pilot plant, three cut fibres constitutes about 0.037% of the total fibres. Therefore, with 0.003% of fibres compromised, a ZW1000© pilot unit was still able to meet an LRV of about 3. This indicates that for a ZeeWeed© water treatment plant producing 1MLD of drinking water (about 725,000 fibres); over 218 fibres have to be compromised before the LRV for B. *megaterium* spores drops below three.

The effect of backpulsing on LRV for the ZW500d© membrane can also be discerned from Figure 5.2, where a drop in LRV was observed after backpulse with one or two pinholes (Figure 5.2, 50 and 65 minutes). This phenomenon is further discussed later in this section. Figures 5.3 and 5.4 demonstrate the relationship between LRV and results of the pressure decay tests during the challenge testing of the membrane pilots. Both membranes appear to exhibit a similar trend in terms of LRV and pressure decay rates with the ZW500d© membrane, showing a larger drop in LRV with increasing pressure decay rates. The rate of drop in the LRV for both membranes appears to slow down with increasing pressure decay rates, indicating that, even when the membranes are severely compromised, they can provide some form of protection against pathogenic microorganisms, equivalent to that of a well-operated direct filtration plant (greater than 3 log removal).

Although the trend of data shown in both Figures 5.3 and 5.4 closely resembles that of an exponential decay, one must resist the temptation of modelling such data. The trend of the data presented in these figures may be applicable to large-scale ZeeWeed© membrane plants. However, further detailed studies and evaluation in large scale is required to verify such an assumption.

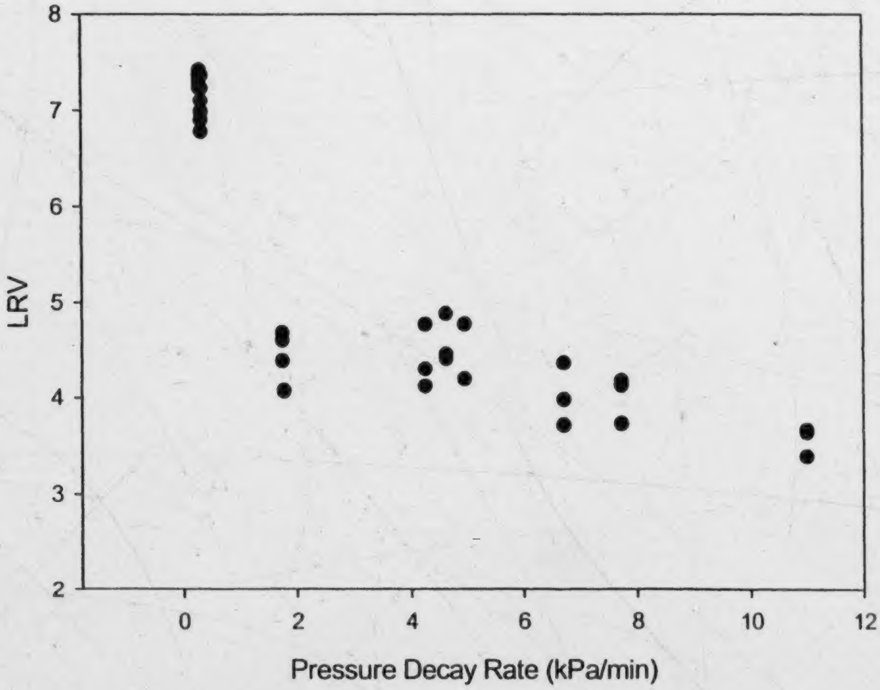


Figure 5.3 The relationship between pressure decay rate and LRV of *Bacillus* spp. spores for the ZW1000© pilot.

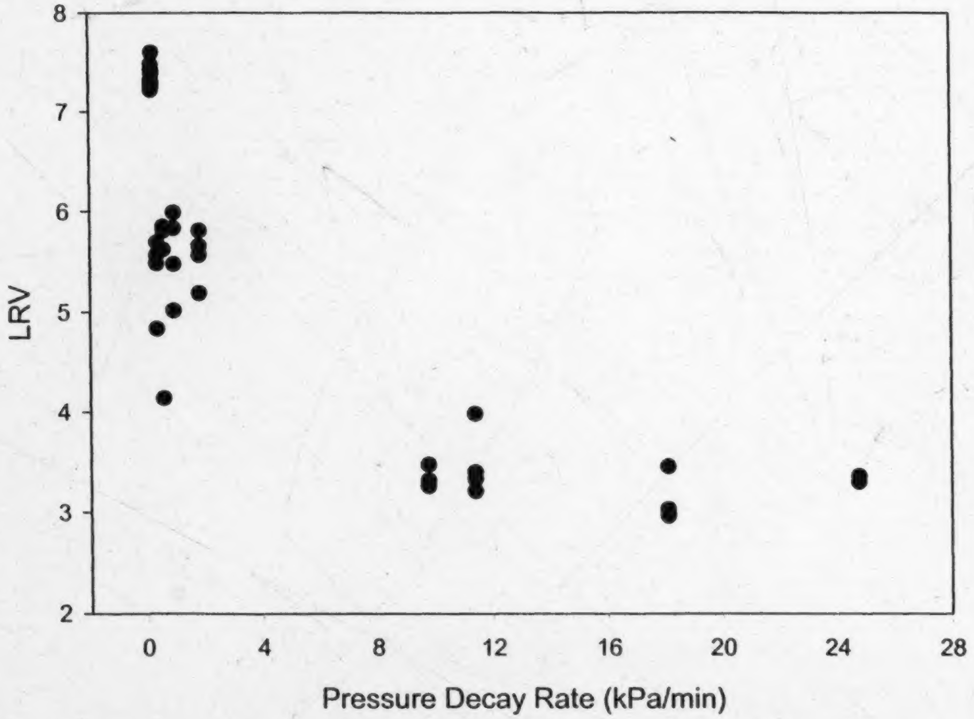


Figure 5.4 The relationship between pressure decay rate and LRV of *Bacillus* spp. spores for the ZW500d© pilot.

Another interesting phenomenon that was discerned from the spore challenge study data was the apparent relationship between membrane backpulse and spore LRV for the ZW500d© pilot plant. The impact of backpulse can be detected in Figures 5.2 and 5.5 in the form of log removal values that differ from those obtained under similar compromised condition (backpulse was performed only with the ZW500d© unit) . Figure 5.5 depicts the impact of backpulsing on LRV that is achieved by the intact and compromised ZW500d© membrane. The impact of the backpulse on the intact membrane appears to be negligible and falls within the standard of deviation for spore enumeration. The impact of backpulse on LRV for the compromised membrane, however, is statistically significant when the fibre is compromised with one or two pinholes. Under such conditions, as depicted in Figure 5.5, LRV following backpulse is consistently lower than that before the backpulse. This phenomenon is somewhat reversed, although not to the same degree, when the breach of integrity is caused by one or more broken fibres. The decrease in LRV of the membrane following backpulse may be attributed to the combined impact of backpulsing on the size of the pinholes and on the concentration of spores in the membrane tank. It is conceivable that a reversal of flow direction during backpulsing (from outside-in to inside-out) temporarily enlarges the pinhole(s) making the integrity breach more conducible to the passage of particulate matter such as *Bacillus* spp. spores. An increase in the concentration of spores in the tank as the result of backpulse, which is depicted in Figure 5.6, also means that there is a higher likelihood of passage of spores (due to higher numbers) through the defect. This effect however, may be somewhat masked by the way LRV is calculated (i.e. higher tank concentrations results in a higher calculated LRV). In addition, backpulsing may reopen a plugged or restricted hole, resulting in increased passage of microorganisms.

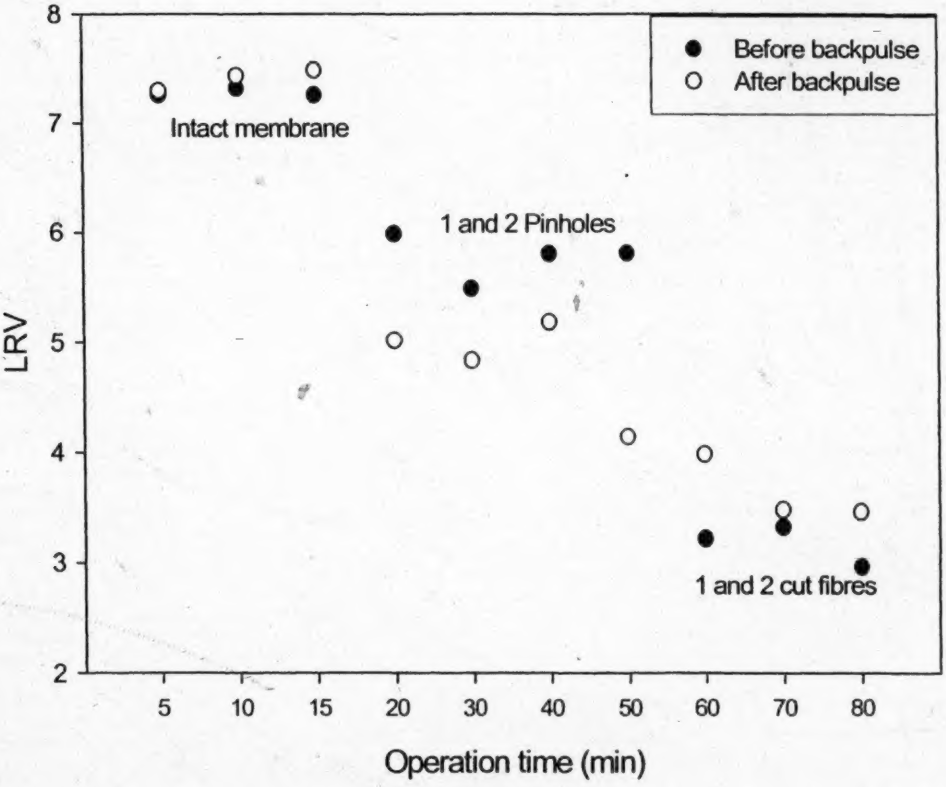


Figure 5.5 Impact of bakcpulsing on the LRV of *Bacillus* spp. spores for the ZW500d© pilot.

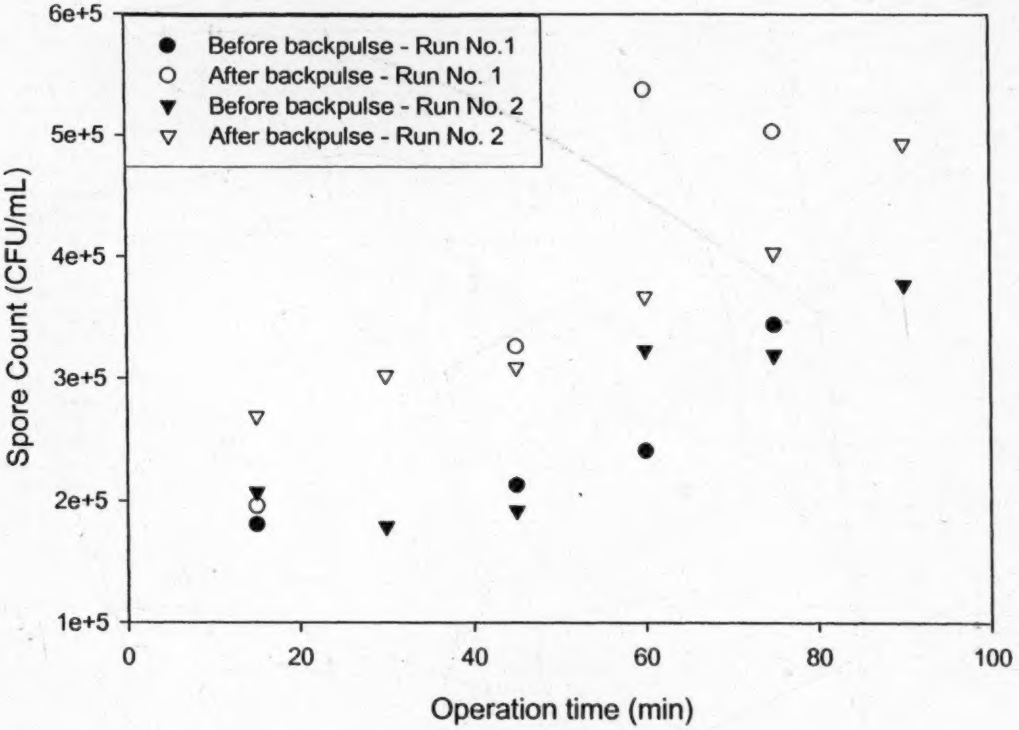


Figure 5.6 Impact of backpulsing on the tank concentration of *Bacillus* spp. spores for the ZW500d© pilot.

5.4.1. Comparison of Measured and calculated LRV

As indicated earlier, many membrane manufacturers also use theoretical models to estimate LRV achieved by a membrane system, based on the results from pressure decay or diffusive air flow tests (Equations 1 and 2). In a recent work Côté et al. (2002) presented a similar relationship for the ZeeWeed© membranes as shown in Equation 6:

$$LRV_e = \log_{10}\left(\frac{Q_{filt} \cdot P_{atm}}{PDR \cdot CF \cdot V_{system}} f_1 \, f_2\right) \qquad [6]$$

where, Q_{filt} is the permeate flow rate (L/min), *CF* is the concentration factor (dimensionless), f_1 is the air-to-water conversion factor (dimensionless, see Equation 7), f_2 is trans-membrane pressure conversion factor (dimensionless, see Equation 8), *PDR* is the pressure decay rate (kPa/min), and V_{system} is the hold-up volume (the volume pressurized by air during the test) (L). The two terms, f_1 and f_2 are estimated by Equations 7 and 8:

$$f_1 = \frac{\mu_{water}}{\mu_{air}} \qquad [7]$$

$$f_2 = \frac{P_{u,test}^{\ 2} - P_{d,test}^{\ 2}}{2 \cdot P_{atm} \cdot TMP} \qquad [8]$$

where, μ_{water} is the viscosity of water (cp), μ_{air} is the viscosity of air (cp), P_{atm} is the atmospheric pressure (kPa), $P_{d,test}$ is the downstream pressure during the test in kPa (for an immersed membrane is determined by the depth of submergence), $P_{u,test}$ is the upstream pressure or the test pressure (kPa) and *TMP* is the transmembrane pressure during filtration (kPa). Using Equation 6, an approximation of LRV can be made based on the results of the pressure decay test. However, Equation 6 has been shown to underestimate the LRV for an intact membrane, because it does not consider the contribution of air diffusion to pressure decay for an intact membranes. Recently, Côté (2003) used a corrected PDR defined as $PDR_{corrected} = PDR_{Measured} - PDR_{Diffusion}$

(Equation 3) instead of PDR in Equation 6 and obtained closer estimates of LRV to those achieved during a challenge test. As indicated earlier, Farahbakhsh and Smith (2003) used a modified version of the Fick's first law of diffusion to estimate the contribution of diffusion to pressure decay for an intact ZW500d© membrane (Equation 4). Using Equation 4 and an average water temperature of 12°C during the challenge testing, the pressure decay rates due to diffusion for the ZW500d©, was estimated to be 0.38 kPa/min. The measured pressure decay rate due to diffusion for ZW500d© during the challenge study was about 0.23 kPa/min. The discrepancy between the measured and estimated values of PDR is most likely due to the effect of submergence on the rate of air diffusion through the intact membrane. A diffusive model for the ZW1000 has not been developed yet. It is therefore safe to assume that the measured pressure decay rates for the ZW500d© and ZW1000© pilot units were primarily due to diffusion. The LRV values for both pilot plants were estimated using Equation 6 and the corrected PDR values (corrected for diffusion) calculated for Equation 3. The results are presented in Figures 5.7 and 5.8. As shown in both figures, correcting the PDR for diffusion provides a closer estimate of LRV for the intact membrane than Equation 6 can alone. This is important since the LT2ESWTR proposes to assign LRV for *Cryptosporidium* spp., based either on the results of challenge study or according to the estimates made by such relationships as Equation 6, whichever is less. The difference between LRV calculated from Equation 6 (without correcting for diffusion) and the measured LRV was over two logs, for both membrane pilot plants.

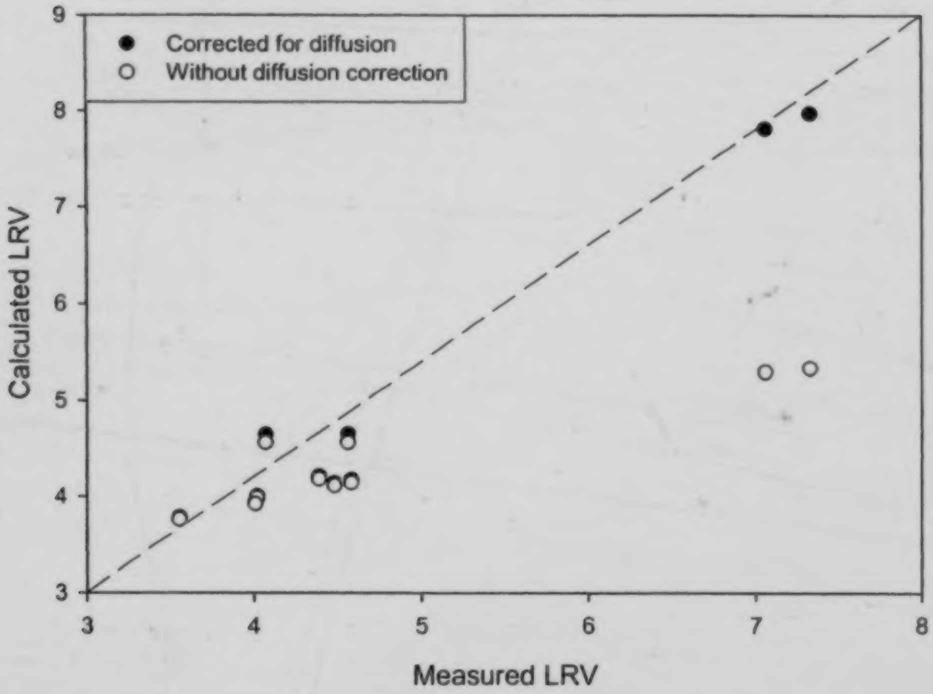


Figure 5.7 Calculated vs. measured LRV for *Bacillus* spp. spores for the ZW1000©.

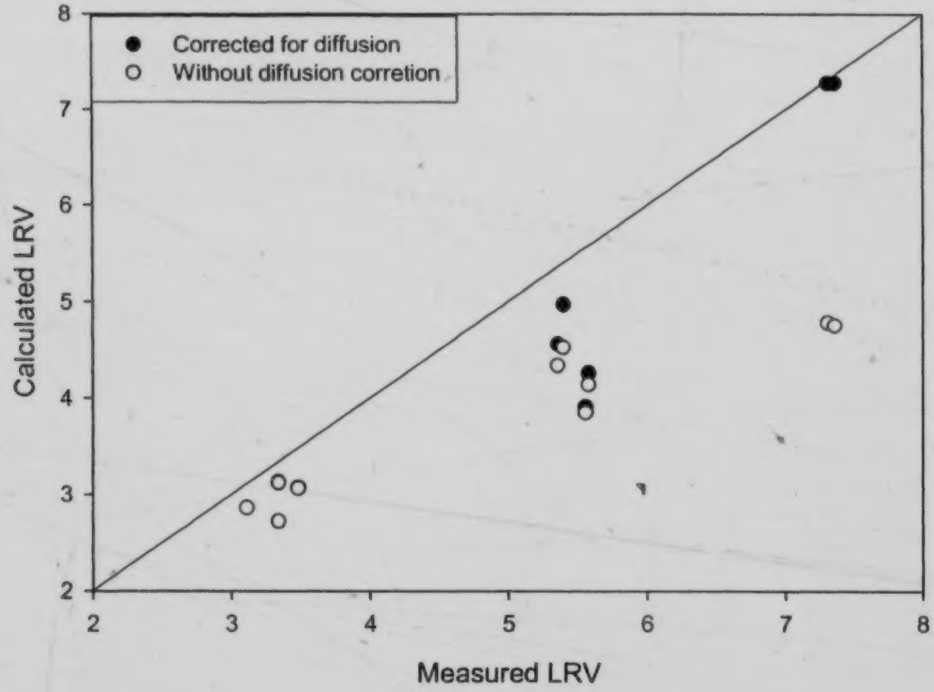


Figure 5.8 Calculated and measured LRV for *Bacillus* spp. spores for the ZW500d©.

5.5. CONCLUSIONS AND RECOMMENDATIONS

Comprehensive challenge testing was conducted on two membrane pilot plants using spores of *Bacillus megaterium*. Both intact membrane pilot units achieved complete removal (over 7 logs) of *Bacillus* spp. spores. Compromising one fibre with one pinhole resulted in the sharpest drop in LRV for the ZW1000© membrane, while the sharpest drop in LRV for the ZW500d© occurred with one broken fibre. This may be attributed to the difference in the inside diameter of the membrane fibres for these membranes. The larger inside diameter for the ZW500d© membrane caused larger volumes of feed water to pass through the broken fibre, resulting in a higher passage of spores. The rate of drop in LRV for an increasingly compromised membrane, showed an exponential decay trend, indicating that the reduction in LRV with increasing number of defects is not cumulative. Both membranes maintained log removal values close to 3, even with a relatively large percentage of compromised fibres. This indicates that even, under sever breach of integrity, the ZeeWeed© membrane can outperform a well-operated granular filtration plant.

For both membranes, LRV dropped noticeably immediately after backpulse, when the breach of membrane integrity was caused by one or two pinholes. The impact of backpulse on membranes with intact or broken fibres was neither negative nor significant. This indicates that, under certain compromised conditions, backpulsing may temporarily reduce the microbial removal efficiency of the membrane tested. Accounting for the contribution of diffusion on the pressure decay resulted in better estimates of LRV for an intact membrane, based on the results of pressure decay tests.

Finally, conducting the spore challenge testing of ZeeWeed© membranes consumed significant amount of time and efforts. About 250 samples were collected and enumerated during this study. The enumeration consumed about 2500 disposable test tubes, 1800 petri plates and numerous pipettes and other consumables. It took about 200 hours of sample preparation and enumeration and extensive effort for spore production. The real cost for such a study, if conducted through a private laboratory, would be considerable and out of reach of most utilities. Alternative, non-biological surrogates, such as latex beads or molecular markers, may be considerably simpler and far less costly for challenge testing of membrane filters.

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CHAPTER 6. APPLICATION OF LATEX MICROSPHERES AS SURROGATES FOR VALIDATION OF MICROBIAL REMOVAL BY LOW-PRESSURE MEMBRANES*

6.1. INTRODUCTION

In the past decade, microfiltration (MF) and ultrafiltration (UF) membranes have enjoyed unprecedented growth in the field of water treatment. Much of this growth has come about because of the proven effectiveness of MF and UF membranes in removing such pathogenic microorganisms as *Cryptosporidium* spp. and *Giardia* spp. The increasingly stringent regulations regarding the microbial quality of drinking water have also encouraged rapid growth of the MF and UF water treatment membranes. According to the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) for a membrane system to receive credits for *Cryptosporidium* spp. removal, its microbial removal efficiency must be routinely verified using direct integrity monitoring tests (USEPA 2001). These direct integrity tests can be classified into two main categories: pressure-driven tests and marker-based tests. The pressure-driven integrity tests, such as pressure decay and diffusive air flow tests, rely on the measurement of pressure drop or air flow rate across an intact wetted membrane. Marker-based tests measure the removal of inert particles in specific size ranges or molecular markers by the membrane and thereby establishing log removal values

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* A version of this Chapter will be submitted for publication to the Journal of Water Supply.

(LRV) for the particular marker. A detailed review of the current integrity monitoring tests was presented by the authors elsewhere (Farahbakhsh et al, 2003).

According to the LT2ESWTR, any of the integrity monitoring tests, pressure-driven or marker-based, are acceptable so long as these tests meet the performance criteria; resolution, sensitivity, and frequency. Resolution has been defined as the ability of the direct integrity test to detect breaches of membrane integrity in the order of 3-μm or less (within the size of *Cryptosporidium* spp.). The sensitivity criterion on the other hand requires that the integrity test be able to verify, as a minimum, the log removal credits that have been awarded to the membrane system. Currently, the LT2SWTR proposes that periodic direct integrity tests be conducted on each membrane module at least once every 24 hours during the operation of the unit (USEPA 2001).

Another requirement of the LT2SWTR is the demonstration of the removal efficiency of the membrane system using challenge testing with *Cryptosporidium* spp. oocysts or a surrogate with removal efficiencies that are not greater than those for *Cryptosporidium* spp. oocysts.

Identification of a suitable surrogate therefore would be beneficial for the membrane industry in the context of direct integrity tests and in lieu of challenge testing with *Cryptosporidium* spp. oocysts. This paper presents the procedure for identification of suitable fluorescent latex microspheres (i.e. beads) as such a surrogate and evaluates its viability for both challenge testing and direct integrity testing of water treatment membranes.

6.2. BACKGROUND

Latex microspheres or beads have been extensively used in tracer studies and for bioassays. Several researchers have investigated the use of latex microspheres as surrogates for transport of *Cryptosporidium* spp. and bacteria in soil and aquifers (Harvey and George 1989; Harvey et al. 1995). In one of these studies, Harvey and George (1989) found that the transport behaviour of bacteria-sized microspheres (carboxylated, carbonyl, or neutral) through a sandy aquifer was substantially different from that of indigenous bacteria. Li et al (1997) investigated the reliability of polystyrene microspheres of 4 to 6-μm in size, as surrogates for *Cryptosporidium* spp. removal. The authors observed a relatively linear relationship between log removals of microspheres and *Cryptosporidium parvum* oocysts by a field-scale, bag filtration system. Similar techniques for enumeration were used for both oocysts and microspheres; this involved filtration of about 5 percent of the effluent with a 1μm polycarbonate membrane, eluting the membrane, concentrating the eluant to between 0.5 and 7.5 mL using a centrifuge, staining *C. parvum* oocysts with an indirect fluorescent antibody, and enumerating the microspheres and oocysts using a hemacytometer. Neutral latex microspheres were used by Bower (1986) to develop a correlation between direct integrity tests and retention of microspheres by a 0.1μm membrane filter. The authors, however, were unable to develop a significant correlation. Acker et al (2001) attempted to assess the integrity of reverse osmosis (RO) spiral-wound membranes with microspheres in a similar size range as that of

MS2 phage. They found that retention of latex microspheres by the RO membranes followed the same pattern as MS2 phage. However, a direct correlation could not be established between the retention of latex microspheres and MS2 phage.

For conducting challenge studies or occasional direct integrity monitoring of water treatment membranes, latex microspheres of appropriate size offer many advantages over biological surrogates such as bacteria spores. Latex microspheres have a very narrow size distribution and typically resist clumping which is observed with bacteria spores. They are available in a variety of sizes, charges and fluorescent colors. They can be economical if purchased in relatively large quantities. Their application does not require skilled operators and they can be easily transported, stored, and samples are viable for long periods of time. There may, however, be several problems associated with using latex microspheres. The main difficulty relates to enumeration of the latex microspheres especially at low counts. Various techniques such as fluorometry, flow-cytometry, capture and enumeration, but with fluorescent microscopy and hemacytometry can be used for their enumeration with varying results. Another difficulty is associated with background noise from other particles with ability to fluoresce. In selecting the appropriate microspheres, several factors must be carefully considered.

6.2.1. Size and Shape

Latex microspheres come in variety of sizes but are often spherical in shape. It is prudent to select a microsphere that is smaller than the microorganism of interest. This would ensure a more conservative estimate of log removal values. Another advantage of selecting smaller microspheres is that the total number of microspheres, in a specific volume, varies with the inverse of the cube of the microsphere's diameter, according to Equation 1 (Polysciences 2000):

$$N = \frac{6W \times 10^{12}}{\pi \rho_p d^3} \qquad [1]$$

where, N is the number of microspheres per mL, W is the weight of polymer per mL in latex (0.025 g for 2.5% latex), ρ_p is the density of polymer in g/mL (1.05 g/mL for polystyrene) and d is the diameter of microspheres in μm. Using Equation 1, the total number of 0.50 μm beads in a 10mL suspension of 2.5% polymer would be about 3.6×10^{12}.

6.2.2. Charge

Latex microspheres are available as negative, positive and neutral particles. The most commonly used microspheres for environmental monitoring are carboxylated beads, with a slightly negative charge. Sulfate modified microspheres carry a stronger negative charge than the carboxylated beads, while amine modified beads carry a positive charge. There are also polystyrene beads that are not charged. The choice of a microsphere with appropriate charge is not an obvious one. In the context of membrane challenge studies, one may choose a microsphere with a similar charge as the microorganism of interest. In most cases, this would be a slightly negatively charged microsphere. However, most membranes surfaces are negatively charged and positively charged beads may provide a more conservative estimate of log removal values.

Other factors that should be considered while selecting suitable microspheres for challenge studies include type of fluorescent dye to minimize background noise and improve detection capabilities, ease of use and storage, and overall cost, which includes the cost of microspheres as well as the cost of enumeration.

6.3. MATERIALS AND METHODS

A variety of latex microspheres with different functional groups and fluorescent dies were purchased from Sigma-Aldrich as well as Polysciences, Inc. The concentrated bead suspensions were supplied in 1 mL, 5 mL and 10 mL volumes and were stored in the dark at 4°C until used. De-ionized water was used for diluting microsphere suspensions. These latex beads are highly uniform with a coefficient of variance of less than 3%. An environmental scanning electron microscopy (ESEM) image of 0.50 μm yellow-orange (YO) fluorescent microspheres is presented in Plate 6.1.

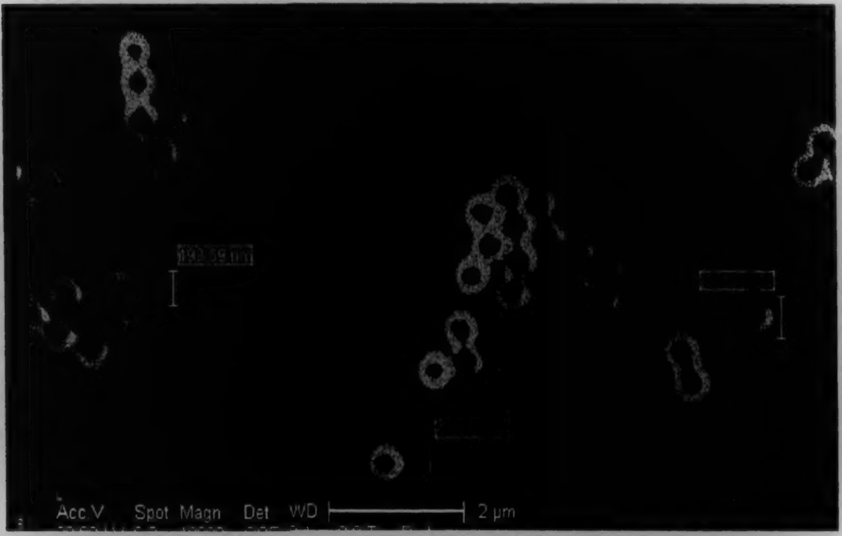


Plate 6.1 SEM image of 0.50μm YO latex microspheres.

Characteristics of latex microspheres used during the study are summarized in Table 6.1.

Table 6.1 Summary characteristics of latex microspheres used during the study.

Dye	Excitation Wavelength (nm)	Emission Wavelength (nm)	Functional groups
Bright blue (BB)	365	435	Carboxylate
Yellow green (YG)	445	500	Carboxylate, sulphate, amine, none
Yellow orange (YO)	535	570	Carboxylate
Polychromatic Red (PC red)	535	588	Carboxylate

The zeta potential of latex beads was measured using a Zetasizer 3000 by Malvern Instruments. Measurement of fluorescent intensity was performed using two different fluorometry instruments. The QuantaMaster Spectrofluorometer Series by Photon Technology International (PTI) and the Turner Quantech Digital Filter Fluorometer by Barnstead Thermolyne Corporation were used to measure the fluorescent intensity of various bead dilutions. Filtration of water samples containing microspheres was performed using 13 mm diameter, 0.22 μm polycarbonate membrane filters and stainless steel filter holders. Fluorescent microscopy work was performed using a Leica TCS-SPS spectral confocal and multiphoton system. Scanning electron microscopy was conducted using a Philips/FEI LaB6 environmental scanning electron microscope (ESEM).

The microsphere challenge studies were conducted at Zenon Environmental membrane pilot facility in Burlington, Ontario. Two different membrane pilot units were used for the challenge study, ZW1000a© and ZW500d©. Both these membranes were hollow-fibre immersed membranes. Characteristics of these membranes are summarized in Table 6.2.

Table 6.2 Summary specifications of membrane pilot plants used during the challenge study

	ZW500d©	**ZW1000©**
No. of modules	3	3
Module's Surface area	31.6 m^2 (340 ft^2)	37.2 m^2 (400 ft^2)
Total surface area	94.8 m^2 (1020 ft^2)	111.5 m^2 (1200 ft^2)
Pore size	0.04 to 0.1 μm	0.02 to 0.1 μm
Inside/outside diameter	0.75 mm/1.95 mm	0.35 mm/0.65 mm
Flux	50 Lmh (30 gfd)	50 Lmh (30 gfd)
Available tank volume	880L	210L
Operation mode	Dead end	Dead end
Recovery	100%	100%
Mixing mode	aeration	Permeate recirculation
Feed	Stored permeate	Stored permeate
Backpulse Flux	50 Lmh (30 gfd)	50 Lmh (30 gfd)
Backpulse Duration	15 seconds	15 seconds
PDT Pressure	62 kPa (9 psig)	69 kPa (10 psig)
PDT Duration*	5 minutes	5 minutes
* PDT = Pressure decay test		

For each challenge test, a 10 mL suspension of 0.5 μm yellow-orange (YO) carboxylated polystyrene beads was diluted with permeate to an appropriate concentration and pumped using a Masterflex peristaltic pump model. Samples were collected from feed, membrane tank, and the permeate at different time intervals for each membrane pilot unit. Challenge tests were performed with intact membranes, as well as membranes increasingly compromised with one pinhole, two pinholes, and one cut fibre. Several 30 mL feed and tank samples and 500 mL permeate samples were collected during the bead challenge study. Feed and tank samples were serially diluted with DI water and several dilutions of each sample (10 mL volumes) were filtered through a 0.22 μm polycarbonate membrane filter. For permeate samples, 100 mL was filtered through the 0.22 μm filter. These filters were then placed on microscope slides with a glass slide cover sealed on top of each membrane. These slides were then enumerated with the use of the Leica confocal system.

6.4. RESULTS

6.4.1. Microsphere Size

It was decided to use a latex microsphere with a diameter of 0.5 μm, representing a conservative surrogate for *Cryptosporidium* spp. (2 to 5 μm) and is equal to the smallest dimension of *Bacillus subtilus* or *megaterium* spores (approximately 0.6 μm wide and 1.4 μm long). Using microspheres of this size also ensures that a challenge study can be conducted economically. A 1 mL suspension of 0.5 μm latex microspheres contains approximately 3.64×10^{11} beads. Therefore, a 20 minute challenge test for a 1 MLD treatment plant at feed concentrations of 1×10^5 beads/L (to test for up to 7 log removal if 100 mL of the permeate is analyzed) requires approximately 1.4×10^{12} beads or about 4 mL of microsphere suspension at a cost of approximately $50 (USD). In comparison, the same challenge test using 1 μm size beads requires approximately 31 mL of bead suspension, at an approximate cost of $380 (USD). This cost may still be affordable for most small utilities, but would discourage frequent use of challenge testing with latex microspheres for direct membrane integrity testing. In comparison, a challenge test using *Bacillus* spp. spores for the same size plant may cost several thousand of dollars just for the supply of spores. Enumeration of samples containing bacteria spores is also far more time consuming and requires highly skilled laboratory personnel.

6.4.2. Microsphere Charge

To determine the surface charge characteristics of latex microspheres with different functional groups, the zeta potential of each type of bead under different pH conditions was measured. The zeta potential of *Bacillus subtilis* spores was also measured and compared with those of microspheres. Results are presented in Figure 6.1. As Figure 6.1 shows, the zeta potential of microspheres with different surface charge (functional groups) does not vary markedly. For all these microspheres, the isoelectric point is between pH 2 to 3. In addition, their electric mobility seems to follow a similar pattern under different pH environments. At pH values typical of most surface waters, these microspheres exhibit zeta potential values that suggest their resistance to agglomeration and clumping. At these pH values, none of the microspheres examined have zeta potential values close to that of B. *subtilis* spores. However, they seem to have higher electrical mobility than the spores, indicating that they may have a lower tendency to adsorb on the surface or pores of a compromised membrane. Consequently, these microspheres may be more conservative surrogates for *Cryptosporidium* spp. than B. *subtilis* spores. The results also indicate that any of the microspheres examined can be used with similar results as surrogates for challenge testing of a membrane, since their zeta potentials appear to follow a similar pattern.

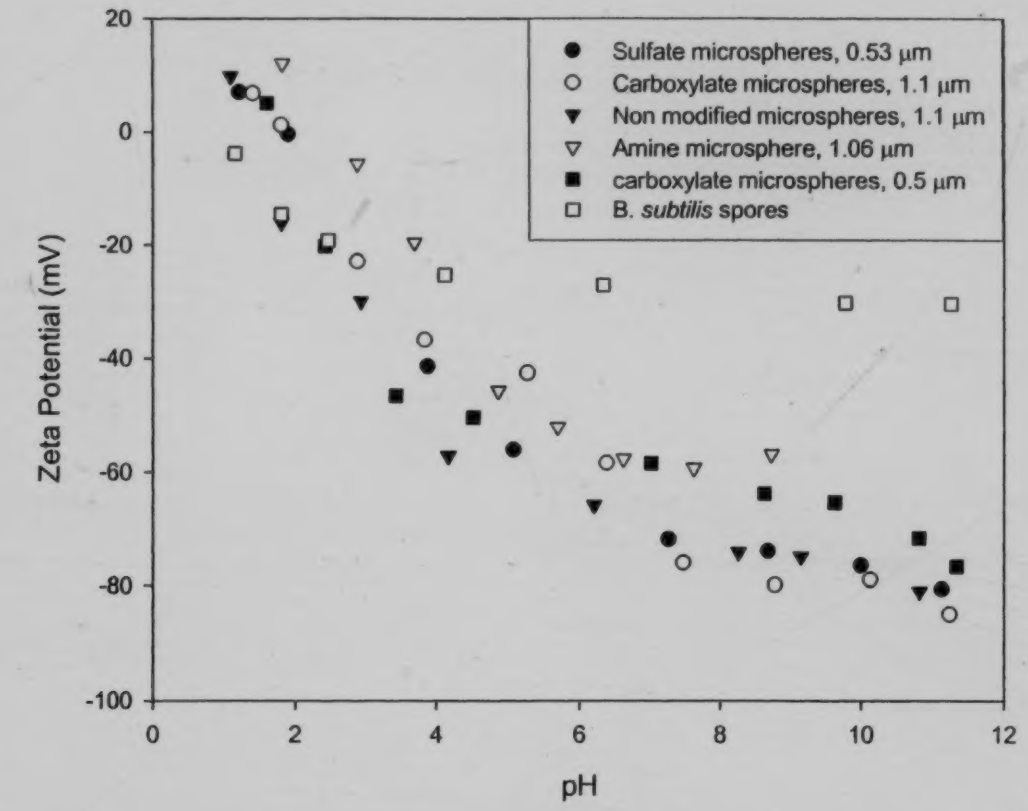


Figure 6.1 Zeta potential profile of different latex microspheres and B. *subtilis* spores.

Other factors may also affect the surface charge and zeta potential of particles. For example, the ionic strength of water may also affect the zeta potential of particulate matter. Figure 6.2 shows the zeta potential of *Bacillus subtilis* spores and 0.5 μm carboxylate latex beads at various concentrations of potassium chloride (KCl). Increasing the KCl concentrations appears to result in more stabilized spores and beads. Therefore, the tendency of latex beads, as well as spores, to adsorb to membrane surface or pores may differ under different water chemistry conditions.

Therefore, the type of latex microspheres (i.e. carboxylate, sulphate, etc.) will not influence the result of a challenge study significantly. In addition, one may expect different results from challenge testing using either latex beads or bacteria spores, under different raw water chemistry. It appears therefore, that the microsphere's surface charge may not be a practical criteria for selecting the suitable type of microspheres for challenge studies, since most microspheres tested exhibited similar electromobility behaviour under different pH environments. This leads to the conclusion that, for conducting challenge testing of membrane filters, the size of microspheres may be a more important parameter than their charge.

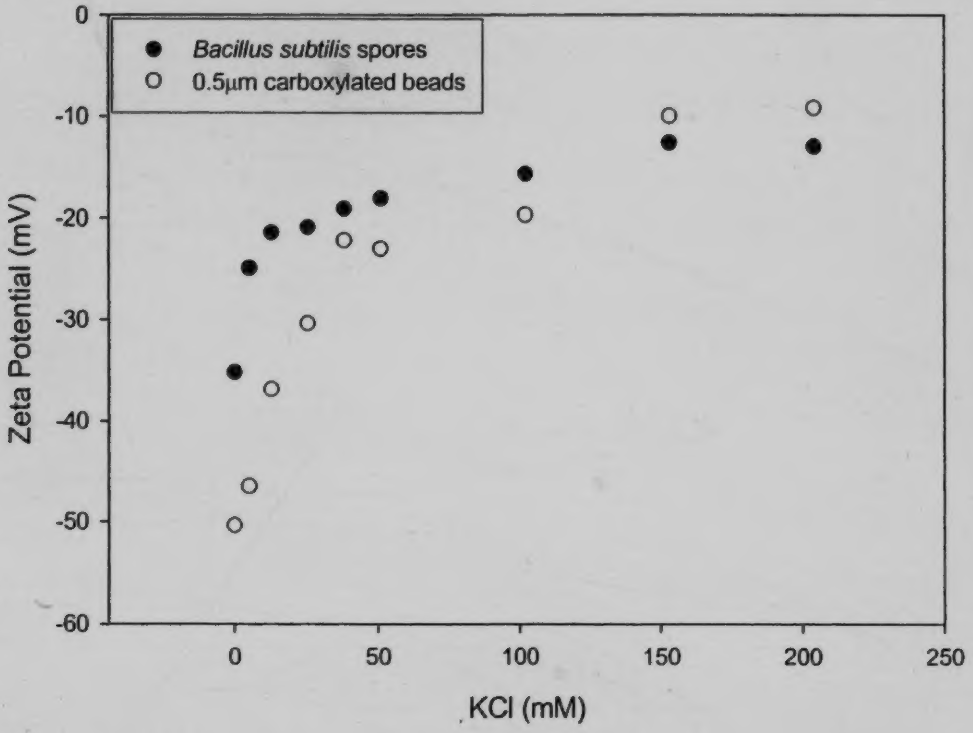


Figure 6.2 Impact of KCl concentrations on zeta potential of *Bacillus subtilis* spores and latex beads.

6.4.3. Method of Analysis

Various methods for determining the concentration or number of microspheres in water samples were investigated including flow cytometry, hemocytometery, flurometry, and confocal laser scanning microscopy. The results are presented below.

6.4.3.1. Flow cytometry

Several water samples containing a known concentrations of latex carboxylate microspheres (1.1 and 0.5μm) were enumerated using a flow cytometer. The flow cytomtery seems to give a sizeable underestimation of beads actually present in the samples. In addition, a flow cytometer could only enumerate very small volumes (1 to 3 mL) within an acceptable time periods (1 to 3 hours). Permeate samples from a challenge test may contain a small number of beads (less than 1 bead per mL) and to reliably enumerate these samples large volumes may be required (up to 100 mL). The inability of the flow cytometer to accurately enumerate the bead samples (less than 1 μm in diameter), coupled with the length of time required to run each samples (over one hour for a 3 mL sample), and resulted in flow cytometry not being selected for enumeration of bead samples. Further improvements in flow cytometry technology may allow this technology to be used for this purpose in future. However, flow cytometry in its present state, may be more suitable for enumerating concentrated bead samples (feed samples perhaps) containing beads with diameters greater then 1μm.

6.4.3.2. Hemacytometry

Several water samples with known amounts of latex beads were enumerated using a hemacytometer. Manual counting of beads, using the hemacytometer, resulted in 98% recovery of the beads consistently. Clearly, hemacytometry appeared to be more accurate than flow cytometry for enumerating latex beads suspensions. However, it would not be suitable for enumerating samples with low bead concentration (less than 1 beads/mL) as the sample volume that can feasibly be enumerated by a hemacytometer is quite small, typically less than 1 mL. Hemacytometry, therefore, may be quite suitable for enumerating feed samples containing large numbers of beads, especially if counting of beads is done automatically, using a particle counting software.

6.4.3.3. Fluorometry

Two different fluorometry instruments were used during this study, one continuous flow unit (QuantaMaster by PTI) and another one with a 3.5 mL cuvette (Turner Quantech). Various samples of bead suspensions with known bead concentrations (from zero to 3.4×10^8) were prepared and analyzed using the two different fluorometers. The unit of measurement for both fluorometers was selected as fluorescent intensity (FI). Latex beads used during this stage included four different fluorescent colours; BB, YG, YO, and PC red. All beads contained carboxylate functional groups. Results from all runs were, for all practical purposes, very similar. Results from one run for a 0.5 μm, YG latex microsphere suspension are shown in Figure 6.3. As the results indicate, the detection limit for the fluorometers was limited to greater than 3.4×10^5 beads/mL. Below this level, the results were within analytical noise. Relatively similar results were obtained for all fluorescent dyes and both fluorometers seem to have the same resolution. Clearly, fluorometry would not be able to detect beads in permeate samples and may have difficulty to accurately enumerate feed samples. Therefore, fluorometry is not considered a suitable method for enumerating water samples from bead challenge testing of low-pressure membranes.

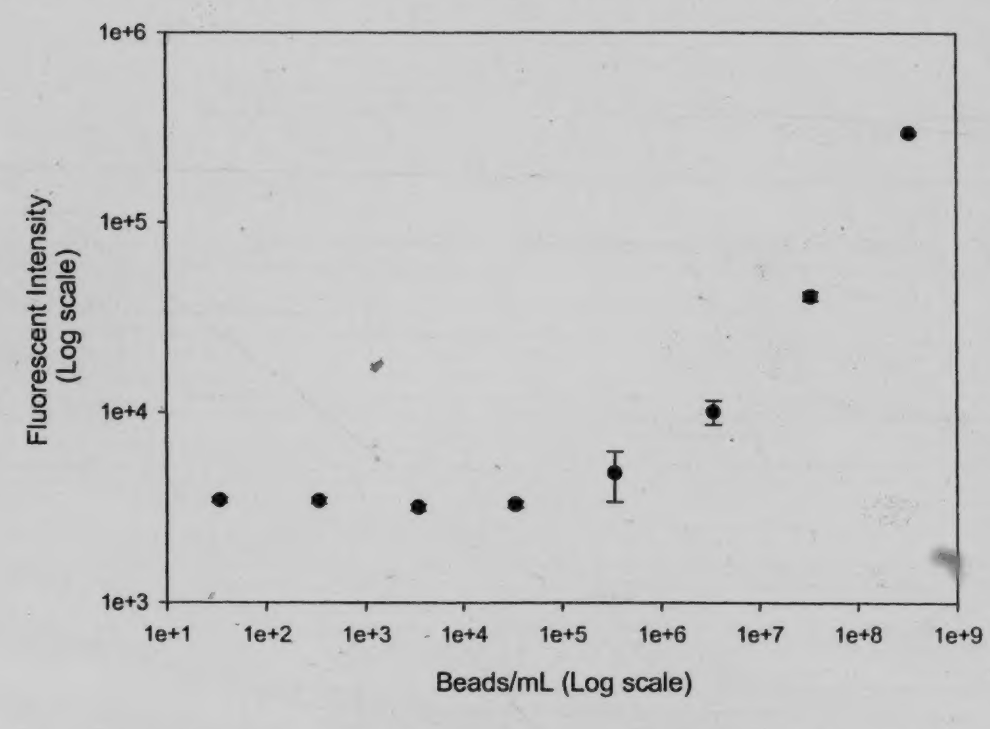
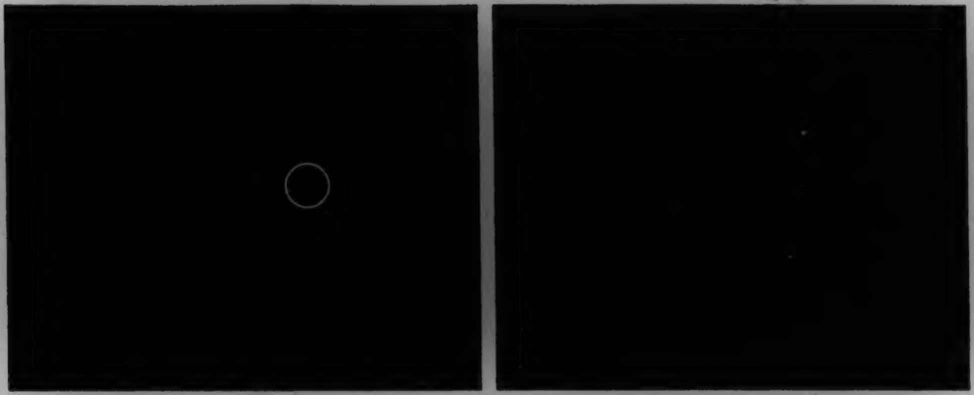


Figure 6.3 Fluorometry results for 0.5μm YG latex microspheres.

6.4.3.4. Confocal laser scanning microscopy

The final method tested for enumerating water samples containing latex beads was confocal laser scanning microscopy (CLSM). Samples containing various types of carboxylated latex beads (BB, YG, and YO) were prepared at different bead concentrations and enumerated using the CLSM. Certain volumes of each sample (depending on expected bead concentrations) were first filtered through 13 mm, 0.22 μm polycarbonate membrane filters, were permanently mounted on a glass microscope slide and enumerated using the CLSM. The CLSM unit is equipped with a particle counting software which enumerated the particles in the specified size and fluorescent colour, make counting of large number of beads relatively easy. The BB beads were not easily visible since their excitation and emission wavelengths fell below the visible light spectrum. Both YG and YO beads however, were readily visible on the filters at even very low concentrations. Several images from each filter were taken and enumerated either manually (low bead concentrations) or using the particle counting software. Plate 6.2 shows two images of the fluorescent bead on the polycarbonate filters, one at 1 bead/mL and the other at 10^8 beads/mL concentrations. The field of view depicted in Plate 6.2 measures 236 μm X 236 μm and was observed at 400X total magnification.



(a) (b)

Plate 6.2 CLSM images of YG latex beads on polycarbonate filters, a) 1 bead/mL, b) 10^8 beads/mL.

As Plate 6.2 shows, the CLSM was capable of detecting as low as 1 bead/mL. The ability to filter the samples on polycarbonate filters allows for detection of down to 1 bead in 100 mL of sample volume. The CLSM, therefore, appears to have adequate resolution for enumeration of samples from membrane challenge studies using fluorescent latex beads.

6.4.3.5. Enumerating the samples from the challenge test

Feed, tank and permeate samples were collected during the bead challenge tests with the ZW1000$^{©}$ and ZW500d$^{©}$ pilot units. These samples were shipped to the University of Alberta for enumeration. During the challenge test, due to the malfunction of the feed pump, it was difficult to accurately dose the membranes. In addition, after the first five minutes of the challenge test, it was observed that the bead suspension was being diluted by the backflow of feed water from the ZW500$^{©}$

unit. These incidents resulted in less than satisfactory challenge study conditions and most likely, prevented the feed concentration from reaching the desired 10^5 beads/mL.

Random tank and feed samples were analysed using the CLSM unit. Most samples showed bead levels far below the expected 10^5 beads/mL. Plate 6.3 shows one image from the feed samples collected during the challenge study.

Plate 6.3 CLSM image of one undiluted feed sample from the challenge study.

According to the above image, the concentration of beads was in the vicinity of 10^3 beads/mL. In addition to difficulties encountered during the challenge study, the long sample storage periods (about 40 days) may have also caused the deterioration of feed samples, resulting in an apparent drop in bead concentrations. No permeate samples from the challenge test were analysed with the CLSM unit.

Due to the difficulties mentioned above, it was not possible to enumerate the samples from the bead challenge tests. However, of all methods that were investigated for enumeration of latex beads, the CLSM proved to be most promising. Additional challenge testing of the same pilot units is planned for the near future to evaluate the suitability of latex beads as surrogates for challenge testing and direct integrity monitoring of low-pressure membranes.

6.5. CONCLUSIONS

Due to difficulties and high costs associated with microbial challenge testing of low-pressure membranes, it is important to identify other low-cost non-biological surrogates for challenge studies. Fluorescent latex beads may offer such an alternative. This study identified several important issues with respect to the use of latex microspheres for challenge testing of low-pressure membranes.

1. Although latex beads are available with different surface charge (different functional groups), it was shown that the presence of different functional groups did not have an important impact on the electrical mobility of the beads. All beads tested exhibited similar zeta potentials under different water chemistry conditions, which were different from the zeta potential of *Bacillus* spp. spores. In addition, the ionic strength of water appeared to impact the zeta potential of latex beads as well as *Bacillus* spp. spores. In general, based on

their zeta potential, latex beads are expected to have less of an affinity to adsorb on membrane surface or pores and hence may be considered a more conservative surrogate for microbial challenge testing of membranes than *Bacillus* spp. spores.

2. The most suitable size for latex microspheres was selected to be 0.5 μm. A number of 0.5 μm beads in 1 mL of commercial bead suspensions is sufficient enough to allow for challenge testing that is affordable to small utilities. In addition, 0.5 μm beads are of the size equivalent to the small dimension of *Bacillus* spp. spores.

3. The choice of dye seems to be dictated by the method of analysis. This study however, seems to indicate that BB latex particles may not be suitable, since their emission and exciation wavelengths are below the visible light spectrum.

4. Most methods used forenumeration of samples containing latex beads failed to accurately determinethe concentration of beads. Hemacytometry, however, may be suitable for enumerating the beads in a sample with relatively large number of beads, such as feed samples. The confocal laser scanning microscopy method appeared to be the most suitable candidate for enumerating beads in low concentration permeate samples. The samples must be filtered first and mounted on a microscope slide, before the actual analysis.

5. Based on the results of this study thus far, the following procedure may be considered for the use of latex beads for challenge testing of low-pressure membranes:
    a. Select 0.5 μm beads preferably with YG or YO fluorescent dyes. Although functional groups do not seem to impact the behaviour of the beads drastically, carboxylated groups may be selected as they are most common and easily available.

    b. During the challenge study, keep the bead suspension well-mixed and ensure sufficient dosing to account for possible adsorption to solid surfaces and membrane surface. Collect at least 300 mL of permeate to allow for enumeration in triplicate.

    c. For enumerating feed samples use either hemacytometry or CLSM with particle counting software. Less than 1 mL of sample is sufficient for enumeration. When using the CLSM method, this volume can be directly placed on a microscope slide without the need for filtration.

    d. For permeate samples, use the CLSM method and filter sufficient volume of permeate sample on a 0.22 μm polycarbonate filter. The filter diameter should not exceed 22 mm, as it would be difficult to place it on a common microscope slide and the inspection of entire filter surface may be quite lengthy.

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CHAPTER 7. REMOVAL OF COLIPHAGES IN SECONDARY EFFLUENT BY MICROFILTRATION – MECHANISMS OF REMOVAL AND IMPACT OF OPERATING PARAMETERS*

7.1. INTRODUCTION

Accessible fresh water resources constitutes about 0.6% of the total amount of water on the planet and of this only a relatively small portion is suited for human use. The scarcity of fresh water supplies around the world has fuelled extensive research into various technologies for the advanced treatment of municipal wastewater for water reclamation and reuse. Membrane separation processes have received considerable attention in the past two decades for the advanced treatment of municipal wastewater. Pathogenic organisms such as protozoa, helminthes, bacteria and viruses are among the most important water quality parameters for water reuse. Total and faecal coliform bacteria have traditionally been used as indicators for fecal contamination of treated effluent. Coliform bacteria, however, may not be the most suitable organisms for evaluating the performance of a MF membrane.

Bacteriophages have been detected wherever fecal contamination by human or other animals occurs (Hargesheimer and Tuer 1990). Bacteriophages are viruses that infect bacteria. Coliphages are bacteriophages that grow and multiply using strains of *Escherichia coli* (E. coli) as host cells. These coliphages have been proposed as indicators of human enteric viruses as well as fecal contamination of source and drinking water (Hargesheimer and Tuer 1990; Sobsey et al. 1995; Grabow 2001). In 2001, the Gold Bar Wastewater Treatment Plant (GBWWTP) located in Edmonton, Alberta decided to investigate the application of membrane filtration for the advanced treatment of secondary effluent. The GBWWTP is an activated sludge plant with biological nutrient removal (BNR). Microorganism reduction of the secondary effluent is done using a medium-pressure UV system. A pilot-scale microfiltration unit was operated from May 2001 to April 2002. The objective was to evaluate the suitability of the permeate from the MF unit for irrigation or reuse as process water in local industries. Of special interest was the evaluation of the performance of the MF unit in removing bacteria and viruses. The research team decided to monitor the removal of native coliphages which were naturally present in the secondary effluent for monitoring the virus removal efficiency of the MF system. The study also investigated the impact of membrane fouling, feed coliphage concentration, and permeate flux on the removal of coliphages by the MF unit and attempted to identify possible mechanisms for coliphage and virus removal by MF. This paper presents the results of MF performance evaluation and discusses the effect of operating conditions and membrane fouling on the removal of coliphages.

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* A version of this Chapter was submitted for publication to the Journal of Water Research, Sept. 2002.

7.2. MATERIALS AND METHODS

7.2.1. Experimental Setup

The experimental setup consisted of a submersible pump to convey the secondary effluent to the feed tank, two 400 μm screens, and the MF pilot plant. A schematic of the experimental setup is shown in Figure 7.1.

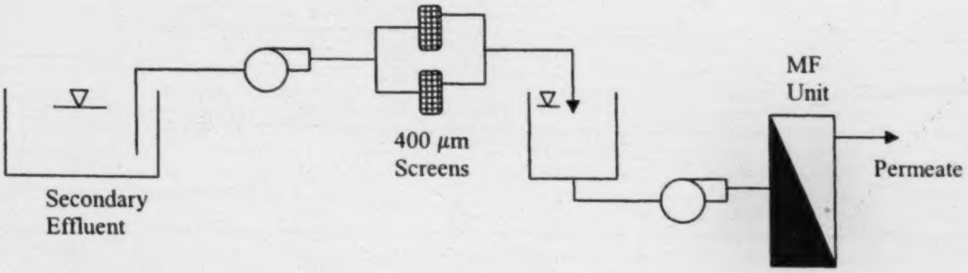
MF
Unit
400 μm
Screens
Permeate
Secondary
Effluent

Figure 7.1 Schematic of the experimental setup

The pilot plant was a 3M10C CMF (US Filter/Memcor) pressurized microfiltration unit consisting of three modules. The pilot plant characteristics are presented in Table 7.1.

Table 7.1 Characteristics of the MF pilot plant.

Nominal Pore Size	0.2 μm
Total Surface Area	45 m^2
Membrane Materials	Polypropylene
Operation Mode	Dead-end , Outside-in
Backwash	Air and water at 18 minutes intervals
Membrane Integrity Monitoring Method	Pressure Decay at 100 kPa once a day
Maximum operating pressure	125 kPa (18 psi)
Permeate flux at 20°C	65 to 85 Lm^{-2}h^{-1}
Chemical cleaning	Caustic wash with Memclean Acid wash with citric acid.

7.2.2. Coliphage Assay

A modified Double Agar Layer (DAL) method, as suggested by Grabow (2001) was used for coliphage enumeration. *E.* coli *C.* (ATCC 13706) was used as the host culture. Large (150 mm) Petri plates were used to enhance resolution of the assay. A brief description of the DAL method is provided below.

1. Prepare bottom agar using 30 g of Tryptocase soy broth (TSB) and 15 g of agar in 1000 mL of laboratory-grade water. Autoclave at 121°C for 30 minutes. Cool in a water bath at 47°C and aseptically pour (approximately 30 mL) into 150 mm Petri plates. Allow solidifying and store inverted.

2. Prepare a fresh overnight (10 to 12 hours) culture of the host bacteria using TSB broth.
3. Prepare the top agar using 30 g of TSB and 7 g of agar, autoclave in an Erlenmeyer flask and keep in a water bath at 47 °C.
4. Add 3 mL of the host culture in 100 mL of top agar, vortex mix, and let stand in the water bath for 3 minutes.
5. Add between 5 to 100 mL of the sample (depending on the expected coliphage concentrations) to the soft agar and host culture, mix gently and keep in the water bath for 3 minutes.
6. Pour approximately 20 mL of the soft agar onto each Petri plate containing the bottom agar. Allow to solidify and incubate inverted at 37 °C ± 0.1 °C for between 8 to 12 hours.

Coliphage assays were performed on both secondary effluent and permeate twice a week. In addition, samples of secondary effluent and permeate were analyzed for fecal and total coliforms, BOD_5, total suspended solids (TSS), turbidity, particle count (2 to 100 μm), conductivity, pH, UV absorbance (UVA), total and orthophosphate (TP, OP), ammonia, TKN, nitrates and nitrites.

7.3. RESULTS AND DISCUSSION

The MF pilot unit produced effluent with high quality as shown in Table 7.2.

Table 7.2. Performance of the MF pilot plant based on permeate quality.

Parameter	Feed	Permeate	Removal
TSS (mg/L)	1.4 to 11.8	0.0 to 0.5	81 to 100%
BOD_5 (mg/L)	0.5 to 6.5	0.08 to 1.5	31 to 96%
COD (mg/L)	2.3 to 51.6	16.5 to 44.1	2.5 to 44.6%
Turbidity (NTU)	1.2 to 5.1	0.09 to1.6	44 to 98 %
Particle Count (No/mL)			
UVA			
TP (mg/l)	0.12 to 3.8	0.07 to 3.6	12 to 60%
TKN (mg/l)	1.4 to 32.8	1.0 to 16.1	7 to 51%
TC (cfu/100 mL)	2.3×10^5 to 2.8×10^6	0 to 7	4.8 to 5.9 logs
FC (cfu/100 mL)	7.2×10^3 to 3.4×10^5	0 to 2	3.9 to 5.3 logs

7.3.1. Coliphage Removal

The overall coliphage removal by the MF pilot plant varied from 0.2 to 3.4 logs. Factors affecting coliphage removal included the extent of membrane fouling and initial coliphage concentrations in the feed. The impact of membrane fouling, feed coliphage concentrations, as well as permeate flux, was further investigated during this study and the results are presented below.

7.3.2. Factors Affecting Coliphage Removal

Several researchers have investigated the mechanism of virus and bacteriophage removal by MF membranes (Jacangelo et al. 1991; Jacangelo et al. 1995; Osumi et al.

1996; Herath et al. 1998; van Voorthuizen et al. 2001). These researchers have identified several factors that contribute to the efficacy of MF for removal of viruses and bacteriophages. These factors include membrane pore size, water chemistry (pH and conductivity); bacteriophage feed concentrations, concentration of particulate matter in the feed, extent of membrane fouling, and presence of cake layer on the surface of the membrane. Several of these factors were not significant during this experiment. These factors included membrane pore size and surface charge (only one type of membrane was used) and water chemistry; feed pH and conductivity remained relatively unchanged throughout the experiments. A set of experimental trials were devised to investigate the effect of other parameters such as feed coliphage concentrations, extent of membrane fouling, and permeate flux on the removal of coliphage by the MF pilot plant.

7.3.3. Impact of Membrane Fouling

To determine the impact of membrane fouling on the removal of coliphages, the MF pilot plant was operated over an extended period of time. Extensive coliphage sampling (four samples within the first 10 hours) was conducted at the beginning of the run, but it was reduced after the first 20 hours of operation to one sample per day. The extent of membrane fouling was also monitored during this run. The drop in specific flux (J_{sp}) over time was used to represent an increase in the extent of membrane fouling. Specific flux is the ratio of permeate flux to transmembrane pressure (TMP). All flux values were corrected to 20°C using the relationships suggested by Karimi et al. (1999). Results of coliphage removal and specific flux during the entire run are presented in Figure 7.2.

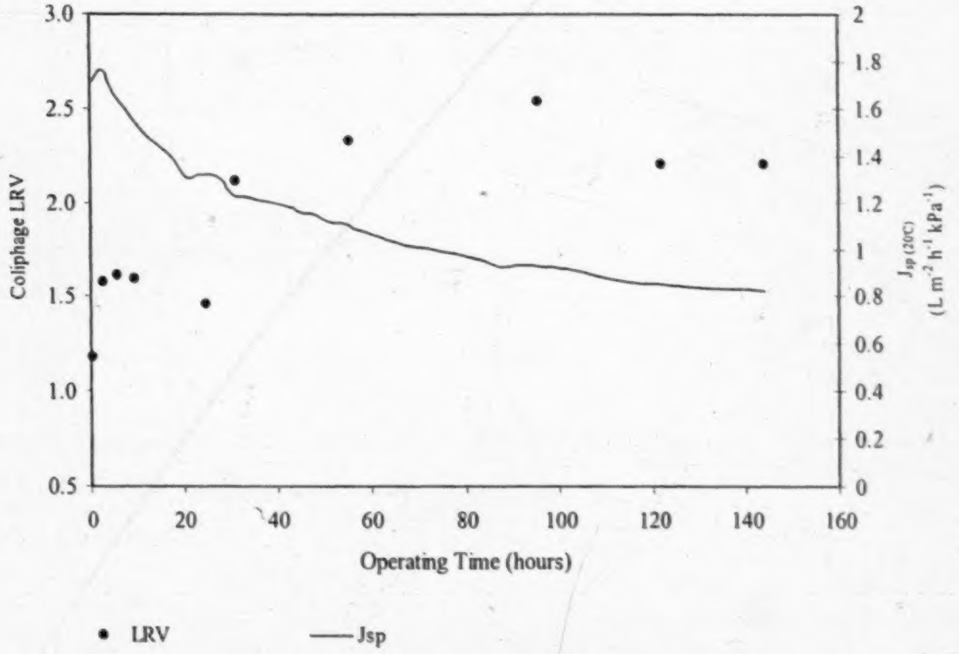

Figure 7.2 LRV for coliphages and specific flux during the entire run

Figure 7.2 shows two distinct plateaus for coliphage removal, corresponding to two different slopes on the specific flux curve. The LRV for coliphage increased rapidly reaching a plateau within the first 20 hours of operation. After 30 hours of operation, the LRV increased again reaching a new plateau. Such a pattern in coliphage removal may be explained based on the different removal mechanisms that are typically attributed to MF membranes. At the onset of the operation, when the membrane is clean, coliphage removal by the MF is primarily due to adsorption on the membrane surface or pores. This mechanism, which is sometimes referred to as the inertial impaction (Osumi et al. 1996), is though to be responsible for the removal of contaminants which are smaller that the filter pores. Interestingly, LRVs dropped slightly after another10 hours of operation, but increased again after 30 hours. This phenomena has previously been observed by Madaeni et al. (1995) and van Voorthuizen et al. (2001) and was attributed by both authors to the reduction in available adsorption sites on the membrane. As adsorption sites are depleted and a cake layer is formed on the surface of the membrane, coliphage removal seems to be predominantly by the cake layer rather than adsorption. The formation of a cake layer on the surface of the membrane resulted in further removal of coliphage and subsequent higher LRVs, as shown in Figure 7.2.

7.3.4. Impact of Feed Coliphage Concentrations

Variations in the concentrations of coliphage in the feed to the MF membrane can also impact the LRV achieved by the membrane. Strictly speaking, as the number of coliphage in the feed increases, the possibility of passage of coliphage also increases. Therefore, one may expect to see higher numbers of coliphage in permeate when filtering an effluent with higher coliphage concentrations. Jacangelo et al. (1995) found that there was a concentration dependence on LRV for MS2 bacteriophage at high phage concentrations (greater than 10^6 PFU/mL). Log removal values for MS2 decreased as phage levels in the feed increased beyond 10^6 PFU/mL. Another study (PDA 1998) indicates that in situations where contaminants are not retained by size exclusion, the outcome may be considered to be probabilistic. The authors go on to say that for a clean membrane, regardless of the challenge level, the probability of passage is the same for any identical particle. The greater the number of particles in the feed, the more likely would be the possibility of passage for some of these particles. The results obtained from this study seem to confirm this for a clean membrane. Figure 7.3 shows the concentrations of coliphage in the permeate vs. those in the feed over an entire operating cycle. As shown, passage of coliphage through the relatively clean membrane seems to be affected by the level of coliphage in the feed. However, such dependency diminished as a foulant layer began to form on the surface of the membrane. Higher removal of coliphage is expected when a cake layer is present on the surface of the membrane, hence masking the impact of the feed coliphage concentrations. This also confirms the assumption that the coliphage removal mechanism for a clean membrane differs from that of a fouled membrane.

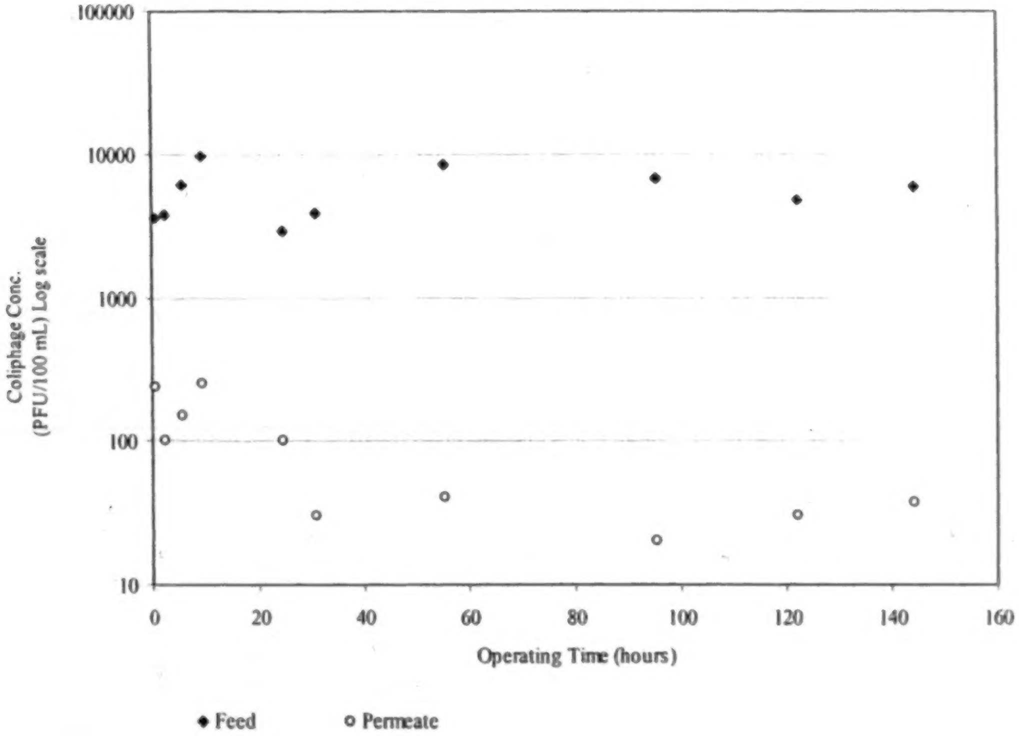

Figure 7.3 Variation in coliphage passage through the membrane as a function of feed coliphage concentrations.

7.3.5. Impact of Permeate Flux

The impact of permeate flux on the removal of coliphages or viruses has not been extensively studied. Applying the probability concept described above, one may conclude that for a clean membrane, the likelihood of coliphage passage should increase with increasing permeate flux. At higher fluxes, the residence time of coliphages in a pore decreases, resulting in a lower probability of coliphage capture. To evaluate the impact of permeate flux on the capture of coliphages, two experimental trials were conducted during the pilot study. One trial was conducted when the membrane was clean (shortly following chemical cleaning). The second trial was conducted when the membrane was fouled (J_{sp} had dropped from 1.76 to 0.73 $Lm^{-2}h^{-1}kPa^{-1}$). Permeate flux was varied from 25 to 85 $Lm^{-2}h^{-1}$ for the fouled membrane and from 25 to 125 $Lm^{-2}h^{-1}$ for the clean membrane. Permeate flux could not be increased beyond 85 $Lm^{-2}h^{-1}$ for the fouled membrane due to excessive increase in TMP. The procedure involved operating the pilot unit at designated flux for two cycles (36 minutes). Samples of feed and permeate were collected at about 10 minutes following the last backwash. All feed and permeate samples were analyzed at the same time immediately after the completion of sampling. Figure 7.4 shows the LRV for coliphages at different flux values for the clean and fouled membrane.

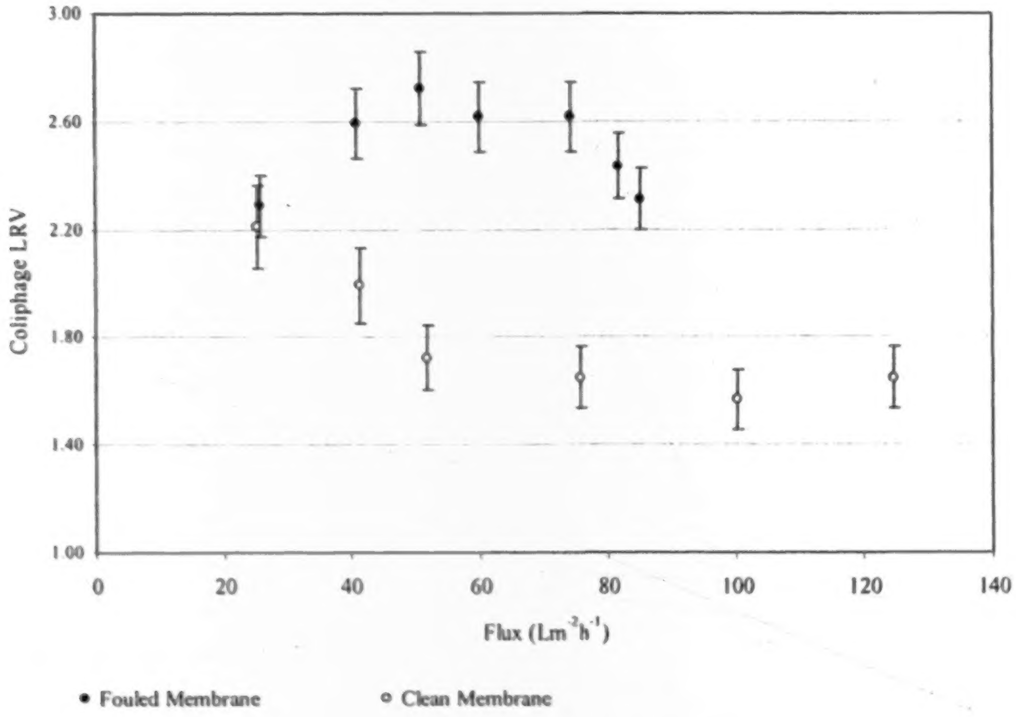

Figure 7.4 Coliphage removal at different flux values for the clean and fouled membrane.

Two distinct patterns for coliphage removal are observed in Figure 7.4. For the clean membrane, LRVs decreased with increasing permeate flux. This was somewhat expected, since as was indicated earlier, the primary mechanism of coliphage removal for a clean MF seems to be adsorption. The likelihood of adsorption decreases with increased permeate flux and consequent decrease in residence time of coliphage in membrane pores.

The impact of permeate flux on retention of coliphage by the fouled membrane was quite different than that with the clean membrane, as shown in Figure 7.4. Removal of coliphages increased at first with increasing permeate flux, reaching a maximum and then decreased as the flux increased further. Such a relationship between permeate flux and coliphage removal for a fouled membrane can be explained. As indicated earlier, when cake layer formation is the main mechanism for fouling, coliphages are primarily removed by the cake layer that is formed on the surface of the membrane. In many cases, cake layers that are composed of materials such as clay or microbial cells, are highly compressible. For compressible cakes, an increase in permeate flux or transmembrane pressure results in a decrease in cake porosity and specific resistance (Mallubhotla and Belfort 1997). Reduced cake porosity, in turn, would result in a higher removal of coliphage by the cake layer. As shown in Figure 7.4, the initial increase in permeate flux and the consequent increase in TMP resulted in reduced cake porosity and higher LRV for coliphages. However, increasing the permeate flux also results in higher shear rates through the pores, dislodging already captured coliphages and releasing them in the permeate. At some point, release of already captured coliphages, due to higher shear rates, exceeds the capture of coliphages by the compressed cake layer, resulting in lower LRV for coliphages.

7.3.6. Comparison of UV and MF for Coliphage Removal

The study also provided the opportunity to compare the efficacy of UV and MF in removing native coliphages in secondary effluent. Figure 7.5 depicts coliphage LRVs for UV and MF during one of the trials. As the figure shows, both MF and UV provided up to 3.4 log removal of coliphages. The removal efficiencies are more or less comparable except at the beginning of the MF operation (relatively clean membrane) where coliphage removal was considerably higher for the UV. As discussed earlier, lower removal efficiencies are expected for a clean MF membrane than for a MF that is fouled.

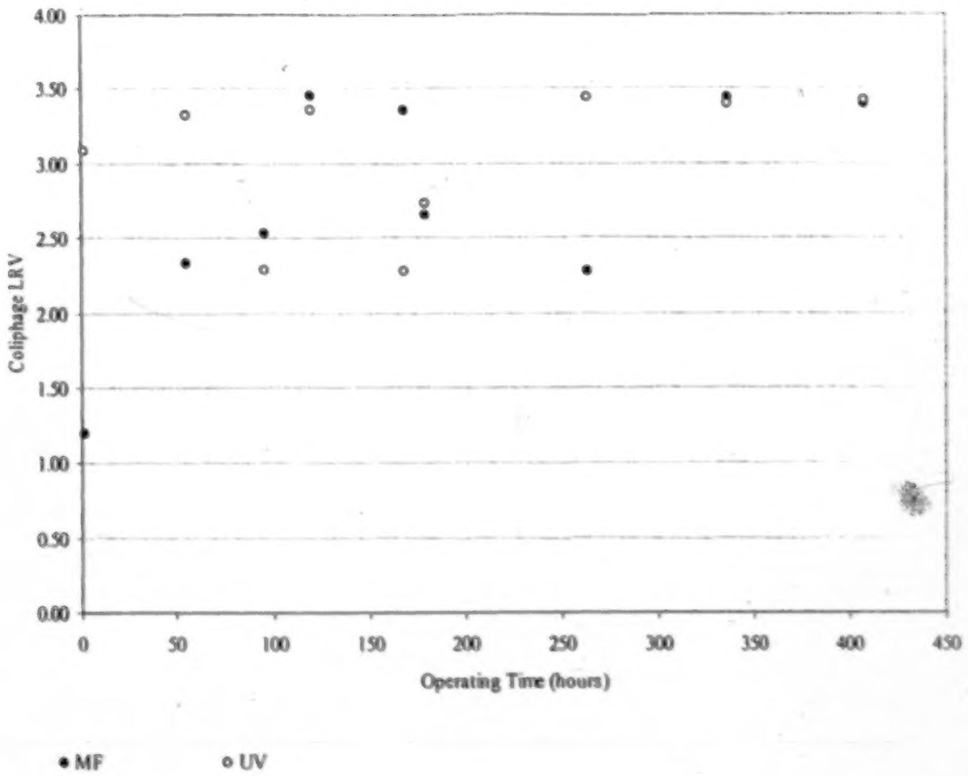

Figure 7.5 Comparison between coliphage LRVs achieved by UV and MF.

7.3.7. Comparing the Removal of Coliphages and Coliform Bacteria

During the pilot study, feed and permeate samples were also collected for faecal and total coliform tests. Coliform tests of final effluent are conducted regularly by the GBWWTP as part of regulatory requirements for effluent discharge. Currently, the WWTP is required to reduce faecal coliforms (FC) to below 200 colony-forming-units (CFU) per 100 mL. High FC removal was expected since these bacteria are generally larger in size than the MF pores. Figure 7.6 shows FC and coliphage removal by the MF for one of the trials. As expected, the complete removal of FC bacteria was achieved in most cases. In comparison, coliphage removal was less consistent and reflected the operating conditions such as TMP and initial feed coliphage concentrations. The results also suggest that native coliphages are better indicators of microbial removal efficiency of a MF than coliform bacteria. This is especially true, when virus removal is concerned (Gagliardo et al. 2000).

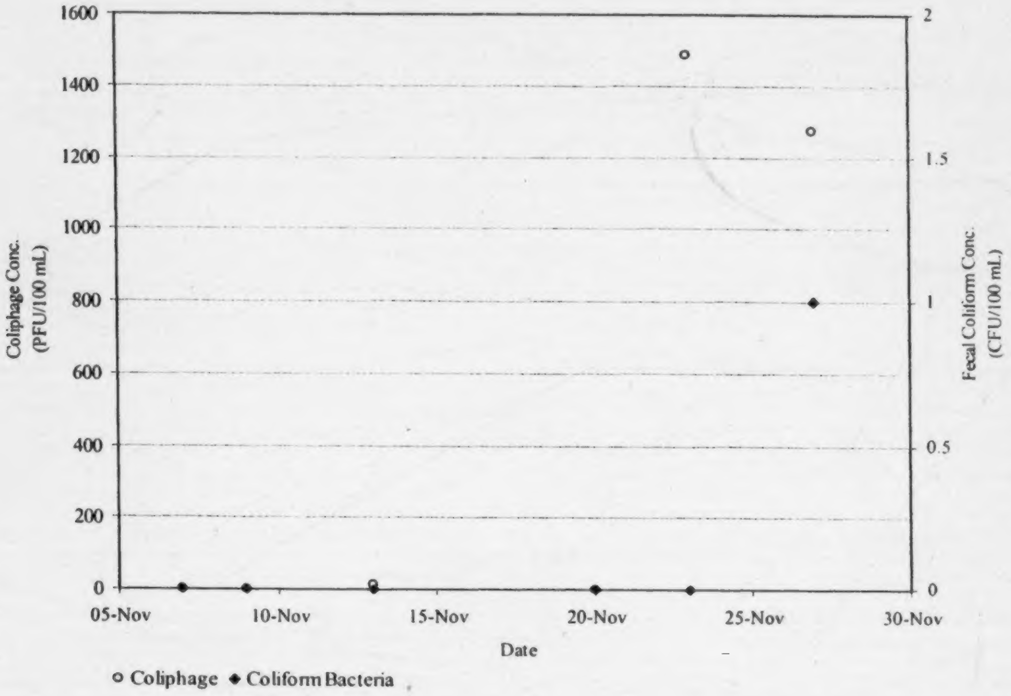

Figure 7.6 Coliphage and fecal coliforms in the MF permeate.

7.3.8. Mechanism of Coliphage Removal by MF

Results obtained from the pilot study provide a relatively clear picture of the main mechanisms involved in removal of coliphages by MF. Inertial impaction caused by adsorptive forces is the primary removal mechanism for a clean MF, resulting in low to moderate removal of coliphages. Inertial impaction is affected by those variables that influence the likelihood of coliphage adsorption such as wastewater chemistry, TMP, permeate flux, and membrane materials. Passage of coliphages through a clean MF is also affected by feed coliphage concentrations; with higher likelihood of passage at higher coliphage concentrations. Inertial impaction seems to be the dominant coliphage removal mechanism only during the first few hours of operation.

As the membrane begins to foul, a compressible cake layer is formed on the surface of the membrane that becomes the primary barrier against the passage of coliphages. Direct interception may be the dominant mechanism for coliphage retention for a fouled membrane. Coliphage removal at this stage is less variable and seems to be only affected by permeate flux and TMP. An increase in permeate flux and/or TMP initially increases coliphage removal by compressing the cake layer and reducing cake porosity. However, further increase in permeate flux causes an increase in shear rates, dislodging captured coliphages and releasing them in the permeate. In this role, membrane fouling becomes beneficial to the performance of the MF membrane as, far as coliphage and virus removal is concerned.

7.3.9. Conclusions

This paper evaluated the removal of coliphages in the secondary effluent by microfiltration at the GBWWTP. It was shown that removal of coliphages varies considerably during the MF operation. Removal efficiencies improved with increased membrane fouling. Removal of FC bacteria, however, was much more consistent with complete retention by MF under most operating conditions. Such a difference stems from different mechanisms governing the removal of coliphages and FC bacteria by MF membranes. The study showed that, for a clean membrane, the primary removal mechanism for coliphages which are smaller in size than the MF pores, is by adsorption following inertial impaction. When pH and conductivity of secondary effluent is relatively unchanged, passage of coliphages through a clean MF is affected by the following parameters:

1. Feed coliphage concentrations. Higher feed coliphage concentrations increases the likelihood of passage of coliphages passing through the membrane, resulting in the release of larger numbers of coliphage in the permeate.
2. Permeate flux. An increase in permeate flux results in a reduced pore residence time and lowers the possibility of adsorption in the MF pores. As flux increases, so does the release of coliphage in the permeate.

It was also shown that membrane fouling was beneficial for removing coliphages by MF. In a fouled membrane, a compressible cake layer is formed that provides the main barrier against the passage of coliphages. At this stage, coliphage removal becomes independent of most operating variables as the governing mechanism changes from inertial impaction to direct interception. Permeate flux impacts coliphage removal in two ways; compressing the cake layer and generating high shear rates. The former helps increase the retention of coliphages by reducing the porosity of the cake layer while the latter lowers coliphage retention by dislodging captured coliphages and releasing them in the permeate.

The results of the study also showed that coliphages in the secondary effluent can act as a better indicator for evaluating the performance of a MF in removing microorganisms, especially viruses, than the traditional faecal coliform bacteria.

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CHAPTER 8. REMOVAL OF VIRUSES BY MICROFILTRATION MEMBRANES – EFFECT OF WATER CHEMISTRY, COAGULATION, AND OPERATING CONDITIONS[*]

8.1. INTRODCUTION

Microfiltration (MF) membranes have enjoyed exceptional growth in the past decade in the water treatment and wastewater reclamation field. The driving force for such rapid growth have been public's concern regarding the microbial quality of drinking water, more stringent regulation with respect to microorganism reduction, and shortage of fresh water supplies that has necessitated wastewater reclamation and reuse. The main impetus in selecting MF membranes has been their ability in removing particulate matter and especially many pathogenic microorganisms of interest to the water industry. From 1996 to 2001, the number of low pressure membrane installations in the United States increased from 26 to 120, many of which were MF membrane installations (USEPA 2001). More recently, application of MF membranes has expanded to areas such as color and natural organic matter (NOM) removal (Vickers et al. 1995; Wiesner and Laine 1996), removal of arsenic (Brandhuber and Amy 1998; US EPA 2000), and pesticides removal (Clausen 2000). Increasingly MF membranes are being installed in existing conventional water treatment plant in place of filtration or in new treatment plants utilizing various chemical pretreatment processes.

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[*] A version of this Chapter will be submitted for publication to the Journal of Environmental Engineering and Science.

Despite their efficiency in removing protozoa such as *Cryptosporidium* spp. and bacteria, MF water treatment membranes have shown great inconsistency in removing viruses. Virus removal values from zero to over 3 logs have been reported for MF membranes (Jacangelo et al. 1995; Jacangelo et al. 1997; Trussel et al. 1998; Schneider et al. 1999). Current regulations in the United States reflect this reported lack of consistency. Only two U.S. states grant MF membranes removal credits for viruses of 0.5 logs.

Reported inconsistencies of MF membranes in virus removal point to the fact that virus removal by MF membranes may be impacted by many variables and should be treated on a case by case basis. This is supported by the available published data of MF virus removal studies. Most studies on MF rejection of viruses have used bacteriophages as surrogates for viruses, which are defined as viruses that infect bacteria and are harmless to humans. For example, van Voorthuizen et al. (2001) showed that hydrophobic interactions between the membrane and bacteriophages was the dominating mechanism for virus removal by a hydrophobic membrane. The impact of pH and conductivity on the removal of bacteriophages was studies by Herath et al. (1999) and as well by van Voorthuizen et al. (2001). Both works showed that the highest rate of virus rejection by MF membranes occurred at the isoelectric point (pI) of the specific virus. Isoelectric point is defined as a condition where the surface charge of a colloid is zero. pH is often the parameter that governs the isoelectric point of a particle and the pH at the isoelectric point is often termed as pH_{pzc}. For example, rejection of MS2 phage was about 80% at its pH_{pzc} of 3.9, compared with only 20% at pH of 6 (Herath et al. 1999). Conductivity was not found to be a significant factor in rejection of phages by MF membranes, although van Voorthuizen et al. (2001) showed that the increase in concentrations of ions (K^+, and Ca^{2+}) improved the removal of phages by the hydrophobic membranes. Other researchers such as Madaeni et al. (1995) point to other factors such as presence of particulate matter (including biomass) or turbidity, cross flow filtration, and lower transmembrane pressures (TMP)as most favourable for virus rejection by MF membranes. Increased virus removal in the presence of other particulate matter is expected, as viruses may attach to larger particulate matter and be removed by straining. Increasing TMP or permeate flux on the other hand, is expected to decrease rejection of viruses as the possibility of adsorption decreases with decreasing retention time. Data by Farahbakhsh and Smith (2003) indicated that increasing permeate flux (or higher TMP) resulted in a decrease in log removal of bacteriophages when the microfilter was clean. A fouled MF membrane, on the other hand, showed increased removal of bacteriophages at higher permeate flux (or higher TMP) due mainly to increased compression of the cake layer on the surface of the membrane.

Another important factor affecting the removal of bacteriophages appears to be membrane fouling (Jacangelo et al. 1995; Farahbakhsh and Smith 2003). It is suspected that the fouling layer on the surface of membrane or the foulants in membrane pores exerts higher resistance to the passage of bacteriophages than does a clean membrane. Both chemical coagulation and electro-coagulation have been shown to improve virus removal by MF membranes (Wiesner and Laine 1996; Zhu et al. 2003). The mechanism of removal is expected to be similar to that of chemical coagulation and filtration, although inactivation of viruses by the electrical current used in electro-coagulation may also contribute to virus removal.

Therefore, from the above review it appears that it is possible to establish optimum conditions for virus removal by MF membranes and that such conditions are primarily dependent upon the dominant rejection mechanisms. Water chemistry parameters, such as pH and presence of ions, for example, impact the adsorption mechanism which is dominant when the membrane is clean. This mechanism may also be affected by TMP and presence of other particulate matter. Chemical coagulation can also be an important factor, both by improving virus adsorption and by agglomerating viruses into larger particulate matter that are removed by physical straining.

This chapter examines the impact of pH, ion content, and coagulation on virus removal by MF membranes and attempts to develop a methodology for optimizing virus rejection by manipulating these parameters.

8.2. MATERIALS AND METHODS

All experiments were performed at the laboratories of the Civil and Environmental Engineering Department at the University of Alberta. Hydrophilic, flat-sheet polyvinylidene fluoride (PVDF) Durapore© MF membranes, with an absolute pore size of 0.1 μm, were used during this study. These membranes were supplied by Millipore. Membrane cells were bench-scale circular stainless steel cells, with center-feed and 50 mm surface area, based on a design by the National Research Council of Canada (Dal Cin et al. 1996). Deionized (DI) water was used throughout the study. Laboratory-grade buffer solutions at desired pH values were purchased for the experiments. All buffers were potassium-based buffers. Reagent-grade potassium chloride (KCl) and calcium chloride ($CaCl_2$) were used to adjust the ion content of the test solutions. For the coagulation trials, reagent-grade alum and ferric chloride were used.

MS2 coliphage (ATCC 15597-B1) were purchased and propagated on *E*.coli host (ATCC 15597) using the double agar overlay technique (DAL) (Adams 1959). MS2 phage was harvested after 24 hours of incubation at 37°C and was stored in a mixture of broth and DI water at 4°C. The same technique (DAL) was used for MS2 phage enumeration.

Propagation of MS2 phage in liquid broth instead of agar plates was also investigated. Flasks containing 150mL of liquid broth (ATCC #271) were inoculated with 5mL of host bacteria and 5mL of recovered MS2 phage. The flask was placed in a shaker bath at 37°C at 200 rpm and samples of the mixed culture were collected at 6 hour intervals for optical density measurements at 600 nm. Optical density dropped from 1.98 to 1.66 after 30 hours and remained unchanged thereafter. MS2 phage was harvested from the liquid broth by filtering the broth through 0.22 μm filters. Phage recoveries were in the same order of magnitude as the agar method. Propagation of MS2 phage in liquid broth is considerably easier than the agar method, both in terms of preparation and harvesting.

The experimental setup is shown in Figure 8.1. A desired titer of MS2 phage was added to the buffered solution at the desired pH and ion content and was stirred gently for 3 minutes. The phage suspension was then pumped to the membrane and permeate was collected in a beaker. Temperature of the suspension was maintained between 21 and 23°C during the entire study. All experiments were conducted in a dead-end mode with no reject stream. Feed and permeate pressures, as well as permeate flow rate, were monitored during each trial using pressure transducers and balances, respectively. All pressure and flow data were recorded using a LabView©-based data logging program.

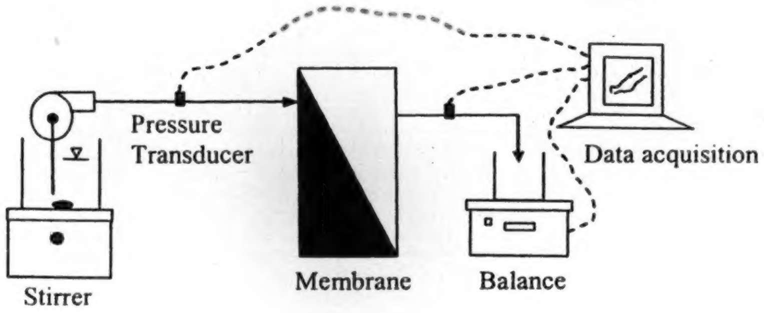

Figure 8.1 Schematics of the experimental setup.

A fractional factorial experiment was designed to determine the impact of pH, mono and divalent ions (K^+ and Ca^{2+}) on the rejection of MS2 phage by the MF membrane. Conducting two-level factorial experiments (levels are defined as high and low) ensures that each level is examined independently with another level of another factor, until all possible combinations have been compared. To reduce the number of experimental trials, the important one or two factor effects are confounded with higher order interactions in what is known as the fractional factorial design. Therefore, a $2^{(3-1)}$ fractional factorial experiment was utilized, resulting in a total of 4 runs. Using centre point replicates, the pure experimental error was estimated without performing replicates of the whole experiment. The pure experimental error was used in the statistical analysis to determine which factors and interactions had significant effects. Four centre-point replicates were conducted for this study. In addition, six additional runs were selected along the three coordinate axes referred to as axial points (Wu and Hamada). These points allow the examination of the region beyond that of normal high and low levels. A total of 14 randomized trials were performed for this stage of the study. Levels of the various factors were set as shown in Table 8.1.

Table 8.1 The factors and levels for the factorial experiments.

pH					K^+ (mg/L)					Ca^{2+} (mg/L)				
-1.41	-1	0	1	1.41	-1.41	-1	0	1	1.41	-1.41	-1	0	1	1.41
1.7	3	6	9	10.3	12	20	40	60	70	12	20	40	60	70
Numbers in the second row reflect the levels for factorial experiments. -1, 0, and +1, are low, center point and high levels, respectively. -1.41 and +1.41 are low and high axial points.														

Values for Ca^{2+} were selected based on typical levels of hardness in surface waters. The low level reflecting soft waters while the high level reflecting very hard waters. Values for K^+ were set to equate those of Ca^{2+}. The response surface method (RSM) was utilized to determine the optimum regions for MS2 phage removal. Three membrane setups, identical to that shown in Figure 8.1, were used side by side during this study. Each set of trials included two normal runs with membrane filters and one control run without any filter. The purpose of the control run was to measure MS2 phage adsorption to surfaces other than the membrane. MS2 phage and several other bacteriophages have a strong tendency to adsorb to solid surfaces and this phenomenon has been reported by other researchers (Acker et al. 2001). Therefore, it was important to ensure that MS2 removal was the result of rejection by the MF membrane and not merely adsorption to different surfaces, such as tubing, tanks, membrane assembly, etc.

Coagulation trials were performed using laboratory grade alum (98% purity) at concentrations of 3, 6, 8, 12 and 15 mg/L. Solution pH was maintained at 6 and no change in pH was observed at the concentrations of alum added. Briefly, MS2 phage was added to the buffered solutions followed by the addition of the desired dose of alum, rapid-mixed for 1 minute, and then fed to the membrane system. Samples collection was initiated after each membrane had filtered about 50 mL of the coagulated solution.

8.3. RESULTS

Most of the initial results from this study were quite unexpected. After repeating the MS2 phage assay several times at different dilutions for all samples, it became evident that there was a strong pH effect on the MS2 phage titres. Up to 4 logs drop in MS2 phage titres was measured primarily due to variations in pH. Figure 8.2 illustrates the effect of pH on MS2 phage concentration in the feed. As is shown, pH has a drastic impact on MS2 phage, one that cannot be easily predicted. Highest MS2 phage titres were measured at pH 6 followed by pH 4. The lowest MS2 titre was at pH 8. Clearly, such results did not allow us to statistically analyze the data from the factorial experiment, since pH effects made the interpretation of the results very difficult. This effect had not been reported by any of the researchers whose work was previously reviewed. A subsequent literature search revealed one reference where similar effects were observed. In a recent work, Price and Van Rooyen (2001) attempted to determine the region of pH stability for a bacteiophage isolated from a polluted water source. They found that the largest region of pH stability (i.e. pH range at which majority of the coliphage remain viable) was centered around a neutral pH, with two other regions around pH of 4 and 12. Variable results were observed at other regions with complete inactivation at pH values less than 3, pH 5, and pH values above 13. This is clearly an important consideration when conducting a challenge study involving MS2 phage. It implies that MS2 phage titres must always be determined following any changes in pH. In addition, to ensure reliable results, any change in pH during the study should be avoided. As a minimum, the pH of solutions containing MS2 phage should always be reported. It is not clear if the effect of pH in MS2 phage is permanent or not. It is possible that MS2 phage may reactivate, if pH is restored to neutral pH, for example.

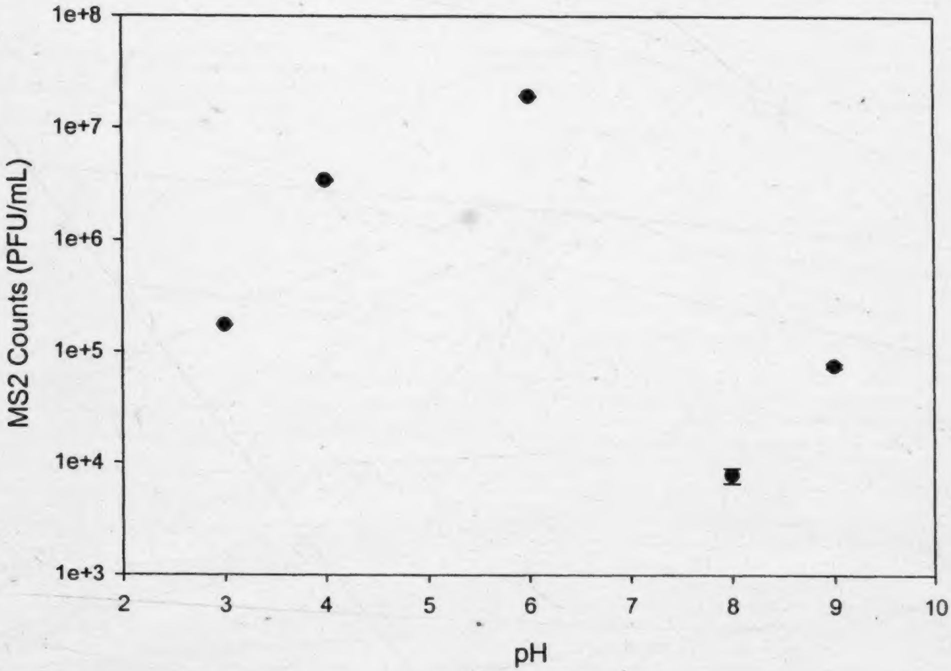

Figure 8.2 Impact of pH on MS2 phage concentration in the feed to the membrane filters.

In addition to the unexpected pH effects, adsorption of MS2 phage on solid surfaces in the setup also complicated the matter. Most researchers that have performed MS2 phage rejection experiments did not seem to account for the effect of adsorption of MS2 phage to surfaces of tubing, tanks, membrane assembly, etc. As indicated earlier, each set of experiments included a control run to measure MS2 phage adsorption to surfaces other than the membrane. The results from the controls indicated that MS2 phage adsorption to other surfaces was considerable at certain pH values. For example, at pH 4, total LRV for MS2 phage was determined to be 0.9 logs. The control run at this pH resulted in MS2 removal of about 0.7 logs, with no MF membranes involved. Consequently, the actual MS2 rejection by the MF membrane at pH 4 was about 0.2 logs, which is slightly higher than the measured standard of deviation of 0.1 logs and, therefore, may be considered insignificant. Considering that 0.2 logs removal at pH 4 was the highest LRV measured during the entire experiment, it may be suggested that the hydrophilic MF membrane used during the experiments did not reject MS2 in a significant way at all the pH values tested. In addition, the presence of varying levels of monovalent and divalent ions (K^+ and Ca^{2+}, respectively) did not appear to have any noticeable impact on the rejection of MS2 by the MF membrane.

The study then focused on the impact of coagulation on the rejection of MS2 phage by the MF membrane. A series of experimental runs were performed by adding alum at 3, 6, 9, and 12 mg/L to the buffered solution containing MS2 phage. Control runs were also conducted to measure MS2 adsorption. The results are shown in Figure 8.3

and indicate that coagulating MS2 phage suspension resulted in increased rejection by the MF membrane. Higher rejection was observed with increasing alum dose reaching a plateau at about 1.0 log. The effect of alum doses higher than 12 mg/L was not investigated during this study. The results however, indicate that, in pure water without any other particulate matter, coagulation results in a maximum removal of about one log beyond 6 mg/L of alum. A higher LRV may be possible at alum doses in the sweep coagulation range, which future studies should investigate. The limited increase in MS2 phage rejection by the MF membrane at relatively small doses of alum may be due to the absence of other particulate matter which would promote further coagulation and may provide sites for MS2 phage adsorption and consequent removal with other coagulated particles.

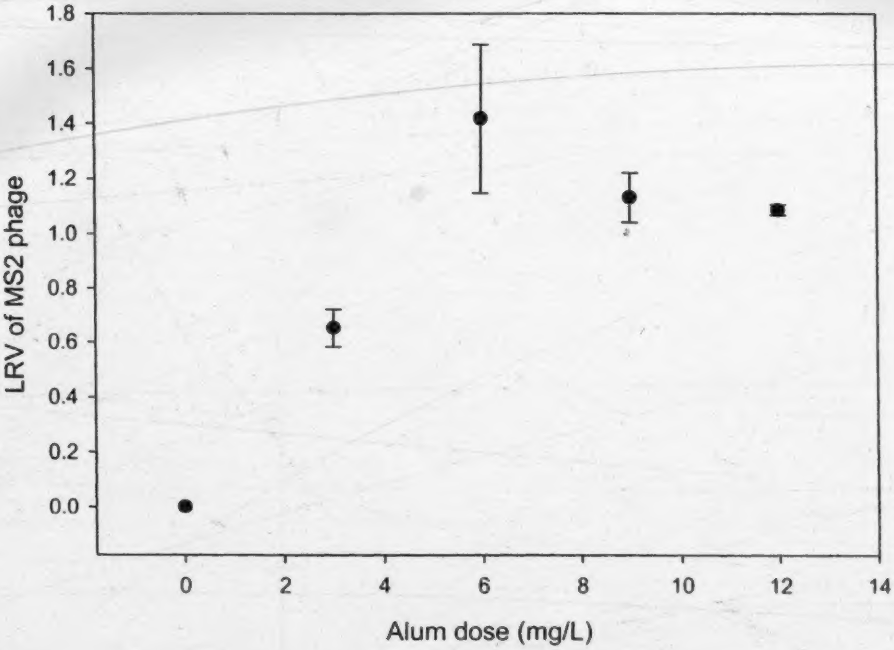

Figure 8.3 The effect of alum dose on LRV of MS2 phage.

8.4. CONCLUSIONS

Several conclusions can be drawn from the results obtained in this study.

1. Variation in pH may have a significant impact on the viability of MS2 phage and can result in a considerable drop in MS2 phage titre.

2. Challenge studies involving MS2 phage should always report the pH of the feed solution and feed samples should always be collected after the point of pH change.

3. Impact of adsorption on MS2 rejection during a challenge test may be significant and should be accounted for during MS2 challenge studies.

4. Without coagulation, ejection of MS2 phage by the hydrophilic MF membrane tested seems to be independent of the pH of solution (between pH 3 to pH 9) and the presence of monovalent or divalent ions. MS2 rejection appeared to be quite insignificant at the pH range studied.

5. Coagulation with alum at relatively small doses resulted in increased MS2 phage rejection by the MF membrane tested. However, in pure water with no other particulate matter, there seems to be a maximum LRV that can be achieved by alum doses between 3 and 12 mg/L. The presence of particulate matter is expected to increase MS2 rejection by the MF membrane, both with and without coagulation.

6. Future studies should evaluate the impact of pH on MS2 inactivation in more detail. In addition, the impact of coagulation at higher does and with and without particulate matter, should be further investigated.

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CHAPTER 9. A REVIEW OF THE IMPACT OF CHEMICAL PRETREATMENT ON LOW-PRESSURE MEMBRANES[*]

9.1. INTRODUCTION

Historically, microfiltration (MF) and ultrafiltration (UF) membranes have been used to treat raw waters with relatively high quality to remove turbidity, particulate matter and microorganisms. Under these conditions, MF and UF membranes were the main unit process with little or no pretreatment. More recently, MF and UF membranes are being installed in water treatment situations where pretreatment is necessary. Membrane water treatment processes that utilize some form of chemical or physical pretreatment can be classified into three major categories.

1. Existing conventional water treatment plants, where MF and UF membranes have replaced sedimentation/filtration or filtration unit processes. The assurance of much higher and more consistent water quality in terms of turbidity and pathogen removal and the ability to increase production in a limited space are the main driving forces for these installations.
2. New water treatment plants that are designed to treat color and reduce total organic carbon (TOC) utilizing chemical and physical pretreatment.
3. Other water treatment/reclamation installations where MF and UF membranes are used in conjunction with other unit processes as pretreatment for processes

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[*] A version of this Chapter was submitted for publication to the Journal of Environmental Engineering and Science, November 2002.

such as nanofiltration (NF) or reverse osmosis (RO). Such installations are referred to as integrated membrane systems.

Chemical and physical pretreatment has greatly expanded the use of MF and UF membranes beyond turbidity and microorganism removal. MF and UF membranes are now being considered for treating high turbidity and high color waters and raw waters containing other contaminants such as arsenic, pesticides, algae, iron and manganese. Integration of MF and UF membranes into existing or newly designed water treatment facilities utilizing chemical or physical pretreatment is relatively recent and as such there are several areas that require further investigation and clarification. These areas include the impact of pretreatment unit processes on the performance of the membranes, chemical compatibility and the impact of chemicals on the membrane life, interaction between chemicals, raw water constituents and membrane materials, impact of integration on membrane operations such as backwash, chemical cleaning, membrane fouling, etc., and the impact of chemicals needed for membrane operation on the overall treatment process.

Chemical or physical processes that may precede MF or UF membranes include coagulation/flocculation, oxidation, adsorption, sedimentation and filtration. This chapter examines the impact of these unit processes on the performance of MF and UF membranes and evaluates the recent developments in this field.

9.2. APPLICATION OF CHEMICAL PRETREATMENT TO MF AND UF

MF and UF membranes are quite effective in removing particulate matter and microorganisms from raw water. Dissolved contaminants, however, are for the most part, unaffected by the MF or UF membranes. Both MF and UF membranes may be used as an effective barrier to remove a variety of chemical contaminants, provided that the proper water chemistry is attained to convert the contaminants to a particulate form. Chemical pretreatment is increasingly used to enhance the removal of a host of contaminants such as heavy metals, taste and odour, pesticides and synthetic organic compounds, and natural organic matter (NOM) from drinking water sources.

9.2.1. Specific Contaminant Removal

9.2.1.1. Arsenic

The United States Environmental Protection Agency (U.S. EPA) has recently lowered the maximum contaminant level (MCL) for arsenic (As) in drinking water from 50 μg/L to 10 μg/L total arsenic, with total arsenic being a combination of As(III) and As(V). Microfiltration and ultrafiltration are viable treatment techniques that would remove particulate and possibly colloidal forms of arsenic, but would have little efficacy in removing dissolved arsenic compounds (Brandhuber and Amy 1998). However, MF and UF, in combination with coagulation, has proven to be an excellent method of removing arsenic from natural waters (Hering et al. 1996; Vickers et al. 1997; Brandhuber and Amy 1998; Nederlof et al. 2000). The strategy for arsenic removal is to incorporate arsenic into ferric hydroxide pin flocs of suitable size for removal by MF or UF (Brandhuber and Amy 1998). Ferric chloride ($FeCl_3$)

coagulation has repeatedly shown better arsenic removal efficiency than alum ($Al_2(SO_4)_3$) coagulation (Chang et al. 1994; Hering et al. 1997; Nederlof et al. 2000). In fact, Chang et al. (1994) found that approximately half the dosage of $FeCl_3$ was required to achieve the same level of removal as alum coagulation in the source water tested. Removal of As(V) during coagulation with $FeCl_3$ is more efficient than As(III) and less sensitive to variations in source water composition, especially at pH values less than 8 (Hering et al. 1996; Hering et al. 1997). As such, arsenic removal was found to be fairly independent of the initial concentration of arsenic in the raw water (Hering et al. 1996). As well, As(III) removal with $FeCl_3$ was found to be adversely affected by the presence of sulphate (pH 4 and 5) and NOM (pH 4 to 9). Alum could not remove As(III) from source water (Hering et al. 1997). Since As(III) is so much more difficult to remove from water than As(V) with $FeCl_3$ coagulation, it has been suggested that oxidation of As(III) to As(V) before coagulation and membrane filtration may be prudent (Brandhuber and Amy 1998). The efficiency of As(V) removal can be increased by increasing the $FeCl_3$ coagulant dosage, as was noted in all the studies, though there is usually a point of diminishing returns.

9.2.1.2. Taste and Odour

The majority of the MF/UF applications in taste and odour (T&O) reduction rely on the use of powder activated carbon (PAC) as a pretreatment step. Taste and odour problems are caused by trace organic compounds such as geosmin or methylisoborneol (MIB), two algal metabolites that have odour threshold concentrations of 4 and 9 ng/L, respectively (Baudin et al. 2001). Other T&O-causing compounds include halogenoanisoles such as 2,4,6-trichloro or tribromoanisole with odour thresholds in the range of 20 to 80 pg/L. MF and UF membranes are unable to remove these compounds solely by size exclusion, but a combination of adsorption with PAC and filtration with UF has proven successful in removing T&O molecules (Baudin et al. 1993; Anselme et al. 1997; Anselme et al. 1999; Baudin et al. 2001; Ford et al. 2001; Schideman et al. 2001). A range of PAC dosages and T&O compound removal has been reported, with PAC dosage dependent on the source water quality and odour-causing compounds (Lâiné et al. 2001). Schideman et al. (2001) varied the PAC dose from 10 to 30 mg/L, resulting in MIB reductions between 49% and 90%, respectively, when the influent MIB ranged from 30 to 150 ng/L. Ford et al. (2001) used PAC at a dose of 20 mg/L and 92% feedwater recovery to reduce geosmin and MIB concentrations to below levels of aesthetic concern (1.8 and 3.6 ng/L, respectively).

9.2.1.3. Pesticides and organic micropollutants

Pesticides and herbicides enter the natural environment mainly from agricultural operations and industrial pesticide production. Because of their widely varying chemical structure and physiochemical properties, pesticides are difficult to remove from the aquatic media. These chemicals are considered ground and surface water pollutants due to their high soil mobility, wide range of solubility, environmental persistence, large-scale application, and toxicity. Effective removal of these micropollutants often requires NF or RO membranes filtration (Hofman et al. 1993; Devitt et al. 1998; Schaep et al. 1998; Bonne et al. 2000; Boussahel et al. 2000; Kiso et al. 2000; Kiso et al. 2001; Van der Bruggen et al. 2001; Kiso et al. 2002). Very few reports on the use of low-pressure membrane processes have been published on the removal of pesticides—even fewer on low-pressure membranes with some sort of pretreatment. Both Clausen (2000) and Mouvet and Jucker (1997) tested the influence of MF on dissolved concentration of pesticides in analytical procedures. Both found that the retention of pesticides varied with filter types and the chemical properties of the pesticides. While Mouvet and Jucker (1997) observed the largest retention for the least water-soluble pesticide, Clausen suggested that pesticides with relatively high solubility and low octanol-water partition coefficients (K_{ow}) can also be strongly retained. It was also noted that the retention of pesticides decreased with increasing volume of pesticide solution passing through the filter, suggesting that once the adsorption sites on the membrane surface are filled, the pesticides would merely flow through uninhibited. Various conventional pretreatment steps may enhance the ability of low-pressure membranes to remove pesticides. Coagulation and solid separation can be used to separate suspensions or colloidal solutions of some pesticides, and may be of some utility in removing the least soluble pesticides (Majewska Nowak et al. 2001). PAC will remove non-polar (hydrophobic) to slightly polar pesticides, though removal efficiency varies widely (Miltner et al. 1989; Baldauf 1993; Hofman et al. 1993; Majewska-Nowak et al. 2001). Competition between organic water pollutants limits the available sorption surface for pesticides. Also, since PAC adsorption capacity for strongly polar pesticides is limited, Hofman et al. (Adham et al. 1993) suggested that PAC addition by itself for pesticide removal is unfeasible. Majewska-Nowak et al. (2001) reported a significant increase in removal of atrazine with MF following chemical pretreatment. While MF alone did not remove atrazine, coagulation with alum or ferric chloride resulted in 30% removal of atrazine. Additional atrazine removal of 52% and 100% was achieved with MF in combination with oxidation (ozone or chlorine) and coagulation or oxidation, coagulation and PAC addition, respectively. The combination of oxidation, coagulation, PAC, and MF was also able to remove 60 to 80% of other organic substances in the water. It should be noted that part of this removal is probably due to the chemical oxidation of atrazine. More work is warranted in investigating the feasibility of chemical pretreatment and MF/UF filtration for the removal of pesticides and micropollutants.

9.2.1.4. Algae and Cyanobacteria

The impact of algae on MF and UF operation has become a concern during periods of algal blooms, where concentrations of algal cells are several orders of magnitude larger than normal (cell counts greater than 300,000 counts/mL, as opposed to a normal of 10 counts/mL). In addition to this, many algae secrete an extracellular, mucilaginous slime material, which has the effect of cementing particulate matter at the membrane surface and increasing resistance to filtration (Montgomery Watson 1997). Several instances of algal bloom-induced fouling have been recorded by Montgomery Watson (1997). A UF plant in France was able to achieve 6-log removal of algal cells, but during this algal bloom (> 17,000 cells/mL) immediate fouling effects were noticed in less than 30 hours, requiring chemical cleaning to restore proper flux levels. In another case, a UF membrane with chlorinated backwash water (3 to 5 mg/L) effectively removed deposited algae cells. At a diamond mine in Australia, MF run lengths were observed to decline to a few days during blooms, but over a five-year period, no long-term performance issues were noted.

In one case the addition of potassium permanganate ($KMnO_4$) to raw saline water before an RO plant eliminated premature fouling problems due to algal cells (Galvin and Mellado 1998). Using this method or the addition of copper sulphate to lyse algal cells may indeed be effective at minimizing membrane fouling; however, this strategy must be re-evaluated when used in conjunction with strains of bacteria or algae that produce intercellular toxins, such as cyanobacteria. One operational strategy for a water utility, then, is to remove the cyanobacterial cells intact, thus preventing the release of the persistent toxins into the water treatment system. Chow et al. (1997a; 1999) found alum or ferric chloride coagulation and flocculation were effective in 3-log removal of cyanobacterial cells without damage to the cell membrane integrity or additional release of intracellular toxins. Further studies with non-pretreated MF and UF systems found that the actual cyanobacteria cells were more difficult to remove from the MF membrane compared to the UF membrane during a backwash (Chow et al. 1997b). If membrane backwashing cannot completely remove the deposited cells, toxins may be released when the cell dies and subsequently passed through the MF/UF membrane. It is hypothesized that coagulation pretreatment to MF and UF membranes may assist in dislodging the deposited cyanobacteria cells during a backwash.

9.2.1.5. Natural Organic Matter

Rejection of natural organic matter by low pressure MF and UF membranes is highly dependant on the individual characteristics of the membrane and the specific characteristics of the natural organic matter (NOM) in the water. Rejection of NOM by membranes is in essence a physical removal process. This means removal of any component is dependent on its molecular volume. However, charged functional groups of the membrane and NOM also play a significant role in rejection (Cho et al. 2000a).

The fraction of NOM that is removed by membranes has typically been the larger-sized humic acid and aromatic components of NOM. Aoustin (2001) found that, for a 10 kDa membrane the highest rejection for humic acid was 75% while fulvic acid rejection was only 41 to 45 %. Cho et al. (2000c) found a positive correlation between NOM rejection and humic acid content. The study suggests that NOM aromaticity/hydrophobicity could be a quantitative predictor of NOM rejection.

Schafer (2000) noted there was a relationship between NOM fouling and NOM rejection by membranes. Increased NOM rejection was observed as the membranes were increasingly fouled. A tight cake structure was found to retain more organics than a loose structure; however, any cake structure retained organics more effectively compared to a cake-free membrane.

The presence of calcium ion has also been noted to increase NOM rejection by UF membranes. Aoustin et al. (2001) found rejection increased from 5% to 70% when calcium ion concentration was raised to 4.0 mM. Without pretreatment, removal of NOM by low pressure membranes is limited and depends on several factors which include nature of NOM, membrane materials, presence of multivalent ions and the degree of membrane fouling. PAC addition and chemical coagulation are the two main pretreatment processes that are often employed with MF and UF membranes for NOM removal. In general, the degree of NOM removal is equivalent to conventional treatment which employs the same pretreatment processes.

9.3. COAGULATION AND FLOCCULATION UNIT PROCESSES

Coagulation and flocculation processes are the main chemical pretreatment steps used in MF or UF water treatment facilities. One of the primary purposes of chemical coagulation pretreatment is to remove NOM and color. As was stated earlier, however, removal of arsenic, taste and odour, iron and manganese, and pesticides has also been targeted. A variety of chemical coagulants have been used in conjunction with MF and UF membranes including alum, ferric chloride, ferric sulfate, aluminium chlorohydrate (ACH) and polyhydroxy aluminium chloride (PACl) (Wiesner and Laine 1996; Best et al. 2001; Braghetta et al. 2001; Schimmoller et al. 2001). In most cases, coagulation has been utilized in direct filtration mode without sedimentation.

To better understand the impact of chemical coagulation on membrane performance, one must appreciate the interaction between NOM, membrane materials and chemical coagulants. The following sections provide a brief description of the interaction between NOM and low-pressure membranes.

9.4. NOM AND LOW-PRESSURE MEMBRANES

NOM is a mixture of macroorganic molecules including biopolymers, proteins, organic acids and bases derived from degradation of biological materials. NOM has been classified into two major groups; humic non-polar (hydrophobic) and nonhumic polar (hydrophilic) material. Functional group analysis of NOM has become important to understanding its interaction with water treatment processes as well as its removal. Greater characterization of NOM will lead to a better understanding of those components of NOM responsible for fouling of membranes and how to mitigate their impact.

9.4.1. Mechanism of NOM Fouling

Mechanisms of NOM fouling of membrane systems have been divided into three categories: cake formation, surface adsorption/deposition of NOM and adsorption/deposition of NOM in the membrane pores (Schäfer et al. 2000a). The majority of the fouling in membranes is caused by partial pore size reduction from foulants adsorbing in the pores. Pores are also blocked by foulants that form a cake and gel layer. Factors that are important in these mechanisms include the specific characteristics of the membrane, the characteristics of the NOM, the ionic strength of the water and operating conditions of the membrane.

Membrane characteristics play a large role in adsorption of NOM as a fouling mechanism. Several researchers, including Howe and Clark (2002), Cho et al. (2002) and Schafer et al. (2000), showed that adsorption of NOM foulants is slightly higher on a hydrophobic membrane compared with hydrophilic membranes.

Many membrane fouling studies have attempted to determine the specific component and characteristics of NOM that actually foul membranes (Jucker and Clark 1994; Cho et al. 1998; Cho et al. 2000b; Cho et al. 2000c; Schäfer et al. 2000b; Aoustin et al. 2001; Howe and Clark 2002). However, there appears to be no general consensus regarding this issue as various studies have come to different conclusions regarding the NOM component responsible for fouling. For example, Aoustin et al. (2001) concluded that hydrophobic UV-absorbing molecules cause irreversible flux decline, while Cho et al. (2000c) found the foulants were larger-size neutral and/or basic NOM components and not the humic substances. Another study by Schafer et al. (Schäfer et al. 2000a) found that humic acid resulted in the highest flux decline (78%) compared with fulvic acid (15%) and NOM (37%). Howe et al. (2002) showed that the small colloidal portion of NOM ranging from 3 to 20 nm in diameter were the important foulants for three MF membranes treating natural water. Adsorption was shown to be an important mechanism for fouling by colloidal NOMs. The presence of calcium ions also appears to enhance fouling properties of NOM (Jucker and Clark 1994; Cho et al. 2000c; Schäfer et al. 2000a; Schäfer et al. 2000b; Aoustin et al. 2001). The major explanation is that calcium acts as a bridge between NOM and the membrane resulting in decreased electrostatic repulsion. It is believed that this allows for a more compact molecule that will fit into the membrane pore and block it.

The above studies indicate that membrane flux decline is dependent on the nature of NOM in water and type of membrane used. Cho et al. (1998) provided evidence for this conclusion. The study found membranes were primarily fouled with hydrophilic or hydrophobic NOM components depending on the dominant action of NOM (hydrophilic or hydrophobic) in the feed water. This indicates that there may be no ideal matching of membrane type with the water to be treated such that membrane fouling is eliminated; rather, there may always be some components of NOM that will foul the membrane.

9.5. IMPACT OF CHEMICAL COAGULATION ON MEMBRANE FOULING

The impact of chemical coagulation on membrane performance has been positive in most cases. Most studies have reported a reduction in the rate of membrane fouling and chemical cleaning frequencies as the result of chemical coagulation (Wiesner et al. 1989; Braghetta et al. 1997; Soffer et al. 2000; Minegishi et al. 2001; Schimmoller et al. 2001; Farahbakhsh and Smith 2002), although some studies indicated that chemical coagulation increased the rate of membrane fouling (Jacangelo et al. 1994; Karimi et al. 1999; Shrive et al. 1999; Schäfer et al. 2001; Shorney et al. 2001). The exact mechanisms by which coagulation pretreatment impacts membrane fouling are not well understood. Several explanations have been proposed which are discussed in subsequent sections.

9.5.1. Increasing particle size distribution

Wiesner (1989) showed that the greatest improvement in flux during microfiltration of a flocculated humic acid suspension coincided with the largest particle diameter produced during flocculation. Similar results were reported by Lee (2000), where reduction of the rate of MF fouling was in part attributed to an increase in particle size to greater than 10 μm as the result of coagulation. The impact of coagulation on increasing the colloid size and hence reducing the rate of fouling of a UF membrane was also highlighted by Lahoussine-Turcaud (1990). Increasing the colloid size may reduce the rate of membrane fouling by several mechanisms. As particle size increases, particle migration away from the membrane wall is also expected to increase, due to increase in lift velocity as shown in Equation 1.

$$v_L = \frac{u_0^2 d_p^3}{32\, \nu r^2} \qquad [1]$$

where v_L is the velocity of particle due to lateral migration, u_0 is the centreline maximum velocity in the hollow fibre, d_p is the diameter of the particles, ν is kinetic viscosity, and r is the radius of the hollow fibre. Increasing particle diameter also enhances particle migration away from the membrane wall by the shear force of the moving fluid. This is demonstrated in Equation 2.

$$v_S = \frac{0.05 u_0^2 d_p^2}{4 r^2} \qquad [2]$$

where v_S is the velocity of particle transport by shear forces.

Additionally, larger particles formed as the result of coagulation and flocculation processes are less likely to penetrate membrane pores and cause pore plugging.

9.5.2. Changing the cake layer morphology and lowering specific cake resistance

Several researchers (Wiesner et al. 1989; Hlavacek and Remy 1995; Lee et al. 2000; Judd and Hillis 2001) have shown that coagulation, under most conditions, reduces the hydraulic resistance of the cake layer that is formed on the surface of a membrane. Lower specific cake resistance generally leads to a reduced rate of membrane fouling. It is proposed that particles formed following coagulation produce a cake layer with a markedly different morphology than those with no pretreatment. In these studies coagulation conditions that resulted in the formation of largest particles (or lowest zeta potential) produced cake layers with the lowest specific cake resistance.

9.5.3. Improving the removal of natural organic matter

As discussed earlier, several investigators have proposed that fouling of MF and UF is predominantly caused by various fractions of NOM that are present in natural waters. Coagulation is known to remove NOM or change the surface chemistry of various NOM species and reducing their affinity to adsorb on the membrane pores or surface. Coagulation with metal ions seems to selectively remove the larger molecular weight, hydrophobic fractions of NOM that are charged with functional groups (Randtke 1988; Crozes et al. 1995). Lahoussine-Turcaud (1990b) observed a reduction in the rate of reversible fouling, due to coagulation which removed relatively high molecular weight humic substances. Membrane fouling following coagulation pretreatment was attributed to smaller-sized polysaccharides that remained in solution. Carroll (2000) investigated the contribution of various components of NOM to membrane fouling. Coagulation with alum (3.2 mg/L as Al^{3+}), with and without settling, greatly reduced membrane fouling as compared with untreated, low-turbidity, high-TOC raw water. PAC pretreatment on the other hand had no noticeable impact on membrane fouling. Reduction in membrane fouling following coagulation was attributed to aggregation of fine particles, increase in particle size, and adsorption or precipitation of dissolved substances and NOM removal. The authors concluded that residual NOM composed primarily of small, neutral, hydrophilic substances were the main contributing factors to post-coagulation fouling. In a detailed study, Howe (2001) investigated the effect of coagulation pretreatment on membrane performance using natural water and bench-scale flat sheet membranes. According to the author the removal of TOC by coagulation could be correlated to reduction in membrane fouling. Lâiné et al. (1990) investigated the effect of coagulation, PAC addition, PAC-coagulation pretreatment on the removal of nonpurgeable organic carbon (NPOC) and fouling control of two different UF membranes (hydrophobic and hydrophilic) using a standard batch stirred, dead-end filtration assembly. Although PAC pretreatment resulted in excellent NPOC removal, it did not improve membrane fouling significantly. Coagulation pretreatment, on the other hand, resulted in the lowest removal of NPOC as compared with the other two pretreatment schemes, but reduced the rate of membrane fouling significantly. Work by Lâiné et al. (1990) shows that, in addition to NOM removal, other factors may have also contributed to reducing the rate of membrane fouling following coagulation. The extent to which NOM removal by coagulation reduces the rate of membrane fouling seems to be dependent on the nature of the NOM, membrane surface charge and hydrophobicity, and type of membrane (MF vs. UF).

9.5.4. Improving backwash efficiency

Farahbakhsh and Smith (2002) showed that coagulation pretreatment reduced the rate of membrane fouling by improving the effectiveness of backwash in removing the fouling layer. Backwash effectiveness in restoring transmembrane pressure (TMP) was higher when chemical coagulation preceded membrane filtration as shown in Figure 9.1. The authors attributed this to the fact that coagulation reduced pore plugging by increasing the size of particulate matter in the raw water. Backwash was more effective in removing a cake layer than dislodging particles that plugged the membrane pores.

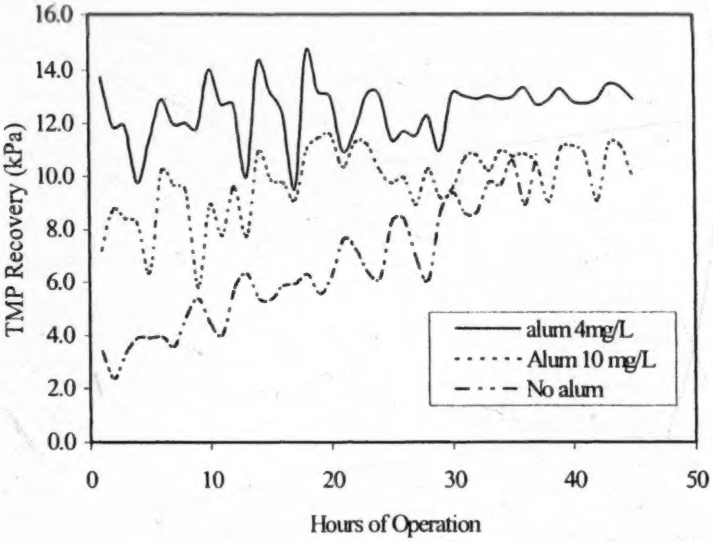

Figure 9.1 Impact of coagulation on the recovery of TMP following backwash.

Judd and Hillis (2001) also indicated that coagulation at specific coagulant concentrations yielded filter cakes that were more readily removed from the membrane surface by backwashing.

9.5.5. Effect of coagulation conditions

Choice of chemical coagulant does not seem to have a noticeable effect on the membrane performance. Most studies indicated that, when metal-based coagulants are used at equivalent metal ion doses, they remove the same amount of NOM and have a similar impact on the rate of membrane fouling (Best et al. 1999; Howe 2001; Judd and Hillis 2001). The effect of mixing conditions and pH has not been clearly established. However, it appears that pH and mixing conditions that produce a flocculated suspension of desired size flocs with near-zero zeta potential may lead to optimum membrane operation. Impact of pH however, may go beyond coagulation optimization. The pH can also impact NOM characteristics and alter the nature of interaction between NOM and membrane materials. Maartens (1999) showed that substantial improvement in UF membrane operation can result by maintaining the pH of natural brown water at about 7 as compared with pH 2 and 9. Coagulant dose seems to also impact the performance of MF and UF membranes. Howe (2001) showed conditions for enhanced coagulation (pH and coagulant dose) resulted in the most improved membrane performance. At lower coagulant doses, the rate of membrane fouling was, in fact, higher than with no pretreatment. A similar finding was reported by Judd (2001) where very low coagulant doses (less than 0.018 mM) resulted in more severe fouling of a MF pilot plant compared with no pretreatment. Lee et al. (2000), on the other hand, found that significantly longer membrane runs were achieved for dead-end MF under charge neutralization conditions (lower pH and coagulant dose) than under sweep coagulation. This was not the case with a cross-flow MF system where flux patterns were similar, irrespective of coagulation conditions. The authors showed that the specific cake resistance was a function of coagulation conditions with charge neutralization producing the lowest specific cake resistance. Farahbakhsh and Smith (2002) also found that a coagulant (alum) dose of 8 mg/L resulted in an increased rate of membrane fouling as compared with a coagulant dose of 4 mg/L, as shown in Figure 9.2. Again the above studies indicate that the impact of coagulation pretreatment on MF and UF membrane may vary greatly depending on the nature of raw water, coagulation conditions, and membrane type and material.

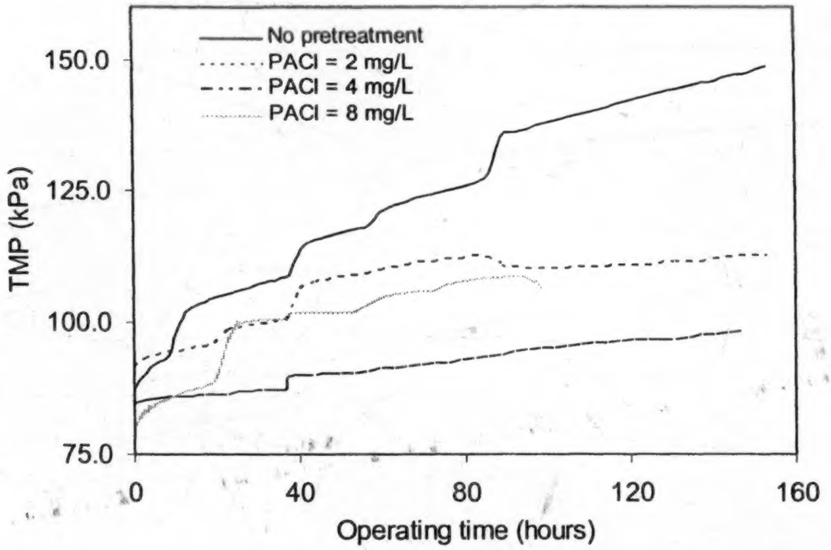

Figure 9.2 Effect of coagulant dose on membrane performance.

9.6. APPLICATION OF POLYELECTROLYTES AND COAGULANT AIDS

Polymer pre-treatment, combined with membranes, has largely been used for specific metal ion removal. These polymers have been engineered to remove a specific metal ion contaminant or for water softening. According to the U.S. EPA (2001), most membranes are anionic in nature and are incompatible with cationic polymers that are frequently used in conventional water treatment to enhance coagulation and flocculation processes. However, Juang (2001) investigated the application of three cationic polymers and regenerated cellulose acetate UF membranes for softening of brackish water and found that the gel layer formed on the surface of the flat sheet membranes were very easily removed. The thickness of the gel layer was a function of the solution pH.

In the area of the application of polymers as a coagulant aid to alum or ferric chloride prior to membrane filtration, very little work has been published. Howe (2001) tested both anionic and cationic polymers as coagulation aids with alum prior to microfiltration. The nonionic polymer did not have any significant impact on DOC removal. The cationic polymer at dosage of 1 mg/L greatly increased DOC removal, and as well reduced the irreversible fouling of the polypropylene membranes. Greater research is needed in this area to fully elicit the impact of polymers addition on membrane filtration performance.

9.7. LIMITATIONS OF COAGULATION PRETREATMENT

Despite the overwhelming evidence supporting the positive influence of coagulation pretreatment on membrane performance, several studies have shown the contrary (Jacangelo et al. 1994; Karimi et al. 1999; Shrive et al. 1999; Schäfer et al. 2001; Shorney et al. 2001). For example, Schäfer et al. (2001) found that coagulation of water containing NOM with ferric chloride resulted in severe fouling of flat sheet MF membranes. The impact on UF membranes was similar but not as severe. The authors also showed that the extent of membrane fouling increased with increasing coagulant dosage. A pilot study conducted by Jacangelo et al. (1994) on hollow-fibre membranes, with three different river water sources, investigated the effect of PAC addition and chemical coagulation on TOC removal and membrane fouling. They concluded that PAC addition at dosages of up to 200 mg/L resulted in the best TOC removal and also slowed down the rate of reversible membrane fouling. On the other hand, although chemical coagulation using alum at concentrations of up to 50 mg/L removed a higher portion of TOC, the impact on membrane fouling was significant. The authors concluded that, for the type of raw water investigated, PAC addition resulted in a much more efficient membrane operation. The cases described in the above literature highlight the fact that coagulation pretreatment of natural waters prior to MF or UF filtration may produce significantly different results, depending on the nature of DOM and membrane materials and configuration.

Other problems reported during coagulation pretreatment of MF and UF feed water include plugging of lumens of an inside-out UF (Guigui et al. 1998) and severe aluminium fouling (Best et al. 2001; Neemann et al. 2001). In the latter case, a sudden change in pH lowered aluminium solubility causing aluminium precipitation on the membrane surface and consequent fouling of the membrane.

9.8. CLARIFICATION UNIT PROCESSES

MF and UF membranes have been extensively used to replace conventional clarification unit processes due to their excellent solid removal properties. Most attempts to integrate MF and UF membranes within conventional water treatment processes have utilized the inline-coagulation MF/UF approach; in some cases, clarification (sedimentation or dissolved air flotation) has been utilized. The primary driving force for inclusion of flocculation/clarification processes has been to reduce the solid load on the membrane and hence improve membrane performance (reduce membrane fouling). This has been particularly the case with source waters high in TOC, color or turbidity. Several researchers have reported on the application of flocculation and sedimentation prior to MF/UF filtration. Braghetta (1997) found that chemical coagulation, combined with DAF prior to MF, increased membrane run lengths, likely due to the reduced solid content and lower concentrations of dissolved organic compounds. In comparison, inline addition of alum without DAF pre-treatment resulted in a decrease in MF membrane run length. Raw water for that study was surface water with low turbidity and intermediate levels of TOC. Minegishi (2001) also found similar results, showing that sedimentation following coagulation significantly reduced the rate of membrane fouling compared with coagulation alone. In another study Braghetta (2001) found that coagulation and clarification resulted in an apparent increase in sustainable flux of 25% to 50% compared with the raw water without pretreatment. Another study involving flocculation solid removal (prefiltration) prior to MF was performed by Kwon (1997). They used a floating medium flocculator/filter prior to microfiltration (flat-sheet) of a kaolinite and fulvic acid suspension. Their results indicated that the MF critical flux was primarily a function of kaolinite concentration and independent of fulvic acid levels. Consequently, the best MF performance was achieved following flocculation/filtration pretreatment.

The review of available literature on clarification pretreatment of MF and UF feed water does not provide any conclusive evidence as to the necessity of clarification prior to MF or UF filtration. Some work indicates that clarification did not provide additional improvement of membrane performance over coagulation/flocculation while other work points to an apparent reduction in the rate of membrane fouling following clarification. Additional research is required to clearly delineate the role and necessity of clarification as a pretreatment to MF and UF filtration of drinking water.

9.9. OXIDATION UNIT PROCESSES

Conventional water treatment plants may utilize oxidants such as chlorine, chlorine dioxide or ozone as an aid to coagulation and flocculation (Singer and Reckhow 1999). In this application, ozone has been much more widely used than other oxidants due to concerns over disinfection by-product (DBP) formation. Pre-oxidation may promulgate microflocculation, where small bubbles of ozone could cause the flocculation of some of the organic matter, allowing the membrane to filter these particulates out of the water. Other applications of oxidation in conventional water treatment include removal of taste and odour, as well as iron and manganese. Various oxidants including ozone, chlorine, and potassium permanganate have been used in these latter instances.

Several studies have examined the effects of ozone on low-pressure membrane filtration performance (Moulin et al. 1991; Takizawa et al. 1996; Hashino et al. 2000; Chang et al. 2001; Hashino et al. 2001; Thompson and Galloway 2001). Chang et al. (2001) used an ozone-ultrafiltration pilot-scale system after a conventional coagulation-sedimentation-filtration process. Ozone doses of 6 to 12 mg/L were used during this study with improved turbidity removal at higher ozone concentrations. In other studies, low doses of ozone (< 0.25 mg/L) resulted in 60% removal of colour-causing organics, while a combination of ozone and ferric chloride ($FeCl_3$)

coagulation enhanced the removal of colour-imparting organics even further (Thompson and Galloway 2001). Hashino et al. (2000; 2001), on the other hand, used an ozone-microfiltration process train with an ozone-resistant polyvinylidenefluoride (PVDF) hollow fibre membrane system. The intent of this study was to use ozone both to improve the water quality and also to obtain a high membrane filtration flux. The membrane filtration flux was improved by ozonation, achieving a maximum flux of 5 $m^3/m^2/d$ with an ozone dose of 3 mg/L, which was three to four times higher than the flux without ozone. However, it was necessary to keep a dissolved ozone concentration of at least 0.3 mg/L at the membrane surface in order to obtain higher permeate flux, (presumably because the ozone prevented foulants from adhering to the membrane surface.) Utilization of ozone in the feed of MF ceramic filters has also prevented organic fouling and resulted in a stable membrane flux. Moulin et al. (1991) found that a residual ozone concentration was required at the surface of the ceramic membrane in order to prevent fouling. An interesting observation from this study was that ozone and aluminium coagulation, when used together, negated the need for frequent backwashing while still maintaining high fluxes. It has also been shown that pre-ozonation is effective in decreasing biofouling of membranes, due to the microorganism reduction effects of the ozone (Takizawa et al. 1996). The authors also investigated the effect of ozone scrubbing at defined intervals rather than plain aeration. Ozone scrubbing was found to be effective in extending the operational periods of membrane filtration. Once a membrane was fouled to a certain extent, however, ozone was not found to be very effective at prolonging the membrane run.

Other chemical oxidants, namely potassium permanganate and chlorine, have also been used in conjunction with MF and UF membranes for the removal of iron and manganese in groundwater sources. Ellis et al. (2000) used a polysulfone MF flat-sheet bench-scale membrane to remove iron and manganese oxide suspensions from a previously oxidized groundwater. Both aeration and potassium permanganate addition were used during the oxidation stage to precipitate the metals in question. The authors indicated that the MF membrane (porosity < 0.1 μm) was quite effective in removing the suspension with very stable permeation rate of 0.5 $m^3/m^2/h$, and the only fouling came from oxide particle deposition on the membrane surface. Addition of potassium permanganate has also been reported by Best et al. (2001) where up to 0.5 mg/L of potassium permanganate was added in combination with alum for the removal of iron and manganese. Takizawa et al. (2001) used up to 0.8 mg/L of chlorine with a hollow-fibre polypropylene MF membrane, to reduce the concentration of manganese from 0.4 mg/L to less than 0.05 mg/L in three different raw water sources. The authors claimed that using chlorine also helped control membrane fouling.

Pre-chlorination has also been used with MF for other purposes. Thompson et al. (1995) used chlorine oxidation followed by MF to successfully remove H_2S, by first oxidizing it to elemental sulphur particles and then removing it by filtration. The authors observed no reduction in flux over a short period of time, but admitted that further testing was required to verify this observation over longer time intervals. In a different experiment, Huang et al. (2001) compared the effectiveness of pre-chlorination and upstream UV-irradiation prior to MF membrane filtration in controlling fouling and production of disinfection byproducts (DBP). While UV delayed the increase of TMP compared to the control run without UV, once biological fouling had occurred the UV-irradiation had little effect. Pre-chlorination was also able to maintain a steady TMP for a long period of time; however, after 60 days of continuous operation the membrane colour changed from white to brown—probably due to manganese fouling—and TMP increased rapidly.

9.10. ADSORPTION UNIT PROCESSES

Several studies have been conducted to evaluate the use of coagulation-PAC with MF or UF membranes (Vickers et al. 1995; Mourato et al. 1999; Baudin et al. 2001; Braghetta et al. 2001; Ford et al. 2001; Schideman et al. 2001). PAC addition following coagulation may be needed to combat seasonal taste and odour problems, high turbidity and TOC levels, or to remove other contaminants. All of the studies reported enhanced the removal of TOC, resulting in lower DBP formation as well as decreased amounts of taste and odour compounds. Laine (1990) investigated the effect of coagulation, PAC addition, and PAC-coagulation pretreatment on the removal of NPOC and fouling control of two different UF membranes (hydrophobic and hydrophilic). PAC-coagulation pretreatment (250 mg/L of PAC, 60 mg/L of poly aluminium chloride) showed the best removal of NPOC as well as reversible fouling control. Most of these studies reported stable permeate flux with some indicating higher flux and lower fouling with coagulation-PAC addition prior to membrane filtration.

9.11. CHEMICAL COMPATIBILITY

Most studies on the impact of chemical pretreatment on MF and UF membranes have focused on contaminant removal and membrane performance (membrane fouling). Little is available in the literature on the compatibility of these chemicals with membrane materials and their long-term impact on membrane's life. Knowledge of the potential problems, as well as the conditions and chemicals that work with certain membranes, is of utmost importance when selecting membranes and treatment chemicals.

Typical pH levels in water treatment plants, such as those found during coagulation, are generally compatible with most membrane materials. Most water treatment membranes operate well within a fairly neutral to slightly acidic pH range, with prolonged extreme acid or alkaline conditions posing potential problems. Most commercially available membranes are resistant to chlorination to some degree, as chlorine is used during operation to combat biological fouling or to remove the foulants during chemical cleaning. Long-term compatibility of MF and UF membranes with other oxidants such as ozone or chlorine dioxide is, in most part, undetermined. Castro and Zander (1993) found that siloxane-coated polypropylene membranes were attacked by 0.2 mg/L ozone at a pH of 5, failing after 18 days of exposure due to chain breaks within the polymer. McCuthchan et al. (1983) found cellulose acetate (CA) membranes to be resistant to low concentrations of ozone for short time periods, although at a higher ozone concentrations, CA membranes may be susceptible to ozone degradation. Hashino et al. (2000) developed a hollow fibre MF membrane made of PVDF, a material that has much better tolerance to ozone than other membranes materials such as polyethylene, polysulfone, and polyacrylonitrile. As mentioned earlier, $KMnO_4$ has been successfully used for iron and manganese removal with different commercial membranes but lack of long-term operating data does not allow a definitive statements regarding its compatibility with MF and UF membranes used in water treatment. From the review of available literature, it appears that most membrane materials in water treatment industry are compatible with commonly used chemical coagulants. Low-doses of coagulant aids and polymers do not seem to adversely impact the service life of commercial low-pressure membranes.

9.12. MEMBRANE PRETREATMENT COSTS

Several studies have assessed the capital and O&M costs of MF and UF plants, with some of the studies including some kind of cost comparisons between MF/UF and conventional treatment systems (Pickering and Wiesner 1993; Wiesner et al. 1994; Sethi and Wiesner 1995; Adham et al. 1996; Gere 1997; Chellam et al. 1998; Jack and Clark 1998; Pianta et al. 2000). While there seems to be a general consensus among authors as to what qualifies for inclusion in the capital and O&M costs, little has been done to address how chemical and physical pretreatment—and the associated reduction in fouling rates—affect the cost of membrane filtration. Most studies that include pretreatment chemicals, such as alum or ferric chloride coagulation, merely state that these chemicals will add to the operating cost of the membrane plant (Wiesner et al. 1994; Gere 1997; Jack and Clark 1998). The cost-benefits of maintaining a higher flux with various levels of chemical and physical pre-treatment is not considered in these studies.

A study by Schäfer et al. (2001) used a unique water quality parameter (WQP) based on colloid, DOC, and cation rejection to describe the product water quality achieved. Estimation of the membrane costs as a function of WQP suggested that UF was superior to MF (a similar cost at higher WQP). However, chemical pretreatment could compensate for the difference between MF and UF. Costs for chemical pretreatment (in this case ferric chloride) were estimated to be above the energy costs for NF if substantial amounts of organics need to be removed. Jack and Clark (1998) state that cost factors other than capital and O&M expenditures need to be considered, such as chemical cleaning frequency and pretreatment. Weisner et al. (1994) indicates that there is a lack of adequate cost histories associated with low-pressure membrane facilities.

In short, membrane filtration applications in water treatment are just evolving past the stage of infancy, and more time is needed to delineate some of the long-term costs and benefits of chemical pre-treatment to the operation of membrane filtration plants. Variable service lives of membranes have been reported anywhere from 5 to 10 years, usually based on cumulative water production; pretreatment with chemicals that change the nature of fouling and the frequency of chemical cleaning soak periods may well have an effect on the reported service lives, but that remains to be seen until several full-scale membrane plants require full module replacement. These knowledge gaps need to be filled in order to comprehensively assess costs and benefits of chemical pre-treatment to low-pressure water treatment membranes.

9.13. PROCESS OPTIMIZATION

Most work on optimization of chemical pretreatment and MF/UF filtration has focused on chemical coagulation. Several researchers (Lahoussine-Turcaud et al. 1990b; Carroll et al. 2000; Lee et al. 2000; Park et al. 2000; Howe 2001; Judd and Hillis 2001) have attempted to determine the limits of effective operation for coagulation and MF/UF membrane filtration of raw water. These researchers have studied variables such as pH, calcium concentrations, coagulant dose, raw water characteristics, membrane materials (hydrophilic vs. hydrophobic membranes), and membrane operational modes (dead-end vs. cross flow). The results of these studies have not been consistent. However, several general conclusions can be drawn from these investigations.

1. Optimization of membrane performance (lowest rate of membrane fouling) was achieved under the same conditions that maximized DOC (UVA) reduction.
2. Conditions for enhanced coagulation generally corresponded to optimum membrane performance. Although in one case, optimum operation of MF membranes corresponded to charge neutralization conditions.
3. Conditions of coagulation that produced a near zero-zeta potential also corresponded to the most optimum membrane performance.

4. No substantial differences were observed between the performances of most commonly used coagulants when dosed at equivalent metal ion concentrations.

9.14. SUMMARY AND CONCLUSIONS

Incorporation of MF and UF membranes in existing or new water treatment facilities for direct or clarified water filtration has been shown to produce very promising results. In this context, MF and UF membranes can be used to treat raw water that has traditionally been difficult to treat with MF or UF membranes such as those high in turbidity and TOC or raw waters containing synthetic organic carbon, pesticides, iron and manganese as well as taste and odour. Most studies utilizing MF/UF membranes in place of clarifiers or filters have shown significant improvement in permeate flux and reduction in the rate of membrane fouling, as well as excellent and consistent permeate quality. Still, several questions remain to be answered.

1. What are the limits of effective operation when MF and UF membranes are integrated in existing or new water treatment facilities? What coagulation conditions can result in the most optimum operation in terms of water quality and membrane performance?

2. What is the long term impact of various chemicals on the service life of MF and UF membranes? What are the upper limits (concentration) for various oxidants, polymers and other chemicals that may be used in conjunction with MF and UF membranes?

3. When would flocculation and sedimentation become necessary?

4. How best can the variety of chemicals, chemical pretreatment conditions, and membrane materials be screened for a specific type of raw water? What standard tests can be performed to help narrow the range of options that are currently available to a utility?

5. How could the performance of various chemical pretreatment options and membrane materials be compared?

6. What are the steps that a utility should undertake when considering to incorporate MF or UF membranes into existing or new facilities for direct or clarified water filtration?

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CHAPTER 10. PERFORMANCE COMPARISON AND PRETREATMENT EVALUATION OF THREE WATER TREATMENT MEMBRANE PILOT PLANTS TREATING LOW TURBIDITY WATER[*]

10.1. INTRODUCTION

Use of low-pressure water treatment membranes, microfiltration (MF) and ultrafiltration (UF), has been steadily growing in the past decade. Much of the growth has been brought about by concerns regarding the microbial quality of drinking water and the ability of UF and MF water treatment processes to remove pathogenic microorganisms from raw water. The ability of UF and MF water treatment membranes in removing particles, turbidity and microorganisms has been well established (Jacangelo et al. 1991; Adham and Jacangelo 1994; Adham et al., 1996; Freeman et al. 1996). In most studies, complete removal of protozoa such as *Giardia* spp. and *Cryptosporidium* ssp. has been achieved. Removal of viruses has been less consistent with UF membranes with log reduction values of up to 5. It has also been determined by several researchers that UF and MF membranes are, for the most part, incapable of removing dissolved organic matter (DOM) from water and that these compounds pass through the membranes unaffected and, in some cases, contribute to membrane fouling (Maartens et al. 1999; Amy and Cho 1999). The reaction between

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[*] A version of this Chapter was published in the Journal of Environmental Engineering and Science, 1(2): 113-122.

DOM and residual chlorine contributes significantly to the generation of disinfection byproducts (DBPs), many of which are suspected carcinogens. With the promulgation of the Surface Water Treatment Rule (SWTR) and anticipated implementation of the Interim Enhanced SWRT (IESWRT) greater restriction is placed on the maximum acceptable concentration of DBPs in the finished water.

The requirement to remove the DBP precursors, coupled with the desire to apply UF and MF membranes to natural waters of increasingly lower quality (higher colour and DOM), necessitate the use of various pretreatment technologies in conjunction with UF and MF. The two most commonly used pretreatment methods for removing DBP precursors are enhanced coagulation and powdered activated carbon (PAC) addition. In addition to removing DOM, PAC and coagulation pretreatment have been shown to reduce or retard membrane fouling and to enhance permeate flux.

The combination of PAC and low-pressure membrane systems has been extensively studied and several mathematical models to predict system's performance have been developed (Adham et al. 1991; Campos et al. 2000; Snoeyink et al. 2000; Jack and Clark 1998). In general, PAC has been shown to be effective in removing smaller size DOM from the feed water and hence reducing the formation of DBP. The impact of PAC addition on membrane fouling, on the other hand, is not well understood. It has been shown by several researchers however, that PAC addition prior to UF can result in significantly longer filtration runs and in some cases may increase the efficiency of chemical washing (Adham et al. 1991). In full-scale applications of the

PAC/UF process, PAC is continuously dosed at a certain concentrations and waste spent PAC is only removed at the end of filtration cycle (Anselme et al. 1997). This allows the concentration of PAC in the system to rise significantly. The residence time of PAC in the system is dictated by frequency of membrane backwashing that can range from 15 to 90 minutes.

The PAC/UF process has also been used for removal of synthetic organic carbon (SOC). A long-term, full-scale study of the PAC/UF process conducted by Yuasa (1998) showed 20 to 75% removal of several types of pesticides at PAC dosage of 2 to 50 mg/L. In another study, Matsui et al. (2001a) developed a model to predict the removal of a trace SOC with PAC/UF process. This model was successfully applied under pilot-scale dead-end and crossflow operations (Matsui et al. 2001b). As well, the PAC/UF has been shown to be effective in removing taste and odour causing compounds such as geosmin and 2-methylisoborneol in addition to removing DBP precursors (Schideman et al. 2001; Ford et al. 2001).

Less extensive work has been performed on the coagulation and UF/MF process. Much of the work has been conducted in conjunction with other pretreatment processes such as PAC addition. Lahoussine-Turcaud et al. (1990) evaluated the effect of coagulation pretreatment for ultrafiltration of surface water using a hydrophobic polysulfone membrane. They found that coagulation of the surface water slowed short-term, reversible fouling, but did not reduce the extent or the rate of irreversible fouling. They also concluded that coagulation pretreatment had its best effect on slowing membrane fouling when coagulation conditions produced particles with a zeta potential near zero. Factors affecting rate of membrane fouling included coagulant dosage, pH, nature of NOM, as well as the calcium content of raw water.

One of the more detailed studies of the effect of coagulation on membrane fouling was conducted by Carroll et al. (2000). Using a single-fibre, outside-in polypropylene microfiltration apparatus, they studied fouling behaviour of the membrane following pretreatment with alum, PAC, and filtration through a 0.2 μm membrane at pH 6. The source water was a surface water with low turbidity and natural organic matter (NOM). Although better DOM removal was achieved with PAC, the rate of membrane fouling was substantially less with alum. Membrane fouling following PAC pretreatment was in fact slightly higher than that of the untreated raw water. The authors concluded that membrane fouling was determined by colloidal materials rather than dissolved NOM. Based on fractionation of various components of dissolved NOM, the authors determined that fouling following coagulation pretreatment was mainly due to the smaller size neutral hydrophilic NOM. This finding is consistent with the fact that most metal-based coagulants are known to preferentially remove hydrophobic rather than hydrophilic substances.

Immersed ultrafiltration enhanced coagulation (IUEC) has been used by Zenon for the removal of colour and DBP precursors in several full-scale applications (Best et al., 1999). Zenon reported higher total organic carbon (TOC) reduction with the IUEC process than can be achieved with the conventional process (based on bench-scale studies). TOC removal in the rangeof 58% to 82% was achieved in various bench-scale studies, while TOC removal of up to 60% was reported under one full-scale operation. A pilot study conducted by Jacangelo et al. (1994) on a hollow-fibre UF membrane with three different river water sources investigated the effect of PAC addition and chemical coagulation on TOC removal and membrane fouling. They concluded that PAC addition, at dosages of up to 200 mg/L, resulted in the best TOC removal and as well slowed down the rate of reversible membrane fouling. On the other hand, although chemical coagulation using alum at concentrations of up to 50 mg/L removed larger portion of the TOC, the adverse impact on membrane fouling was significant. The authors concluded that for the type of raw water investigated, PAC addition resulted in a much more efficient membrane operation.

Another detailed bench-scale study of coagulation/microfiltration was conducted by Lee et al. (2000) for three different MF systems, dead-end MF (pressure system), dead-end immersed MF, and cross-flow MF. The study concluded that best TOC removal (35.3%) was achieved for all three systems under coagulation conditions in the charge neutralization region (pH of about 5 and alum dosage of between 5 to 20 mg/L). In contrast, conditions corresponding to sweep coagulation resulted in lower TOC removals (up to 23.5%). In addition, significantly longer membrane runs were also achieved for the dead-end MF under charge neutralization conditions than sweep coagulation. This, however, was not the case with cross-flow MF system where flux patterns were similar irrespective of coagulation conditions. The authors showed that the specific cake resistance is a function of coagulation conditions with charge neutralization producing the lowest specific cake resistance. It appears from this study that it is beneficial to optimize coagulation pretreatment at the region of charge neutralization, to ensure longer membrane runs (duration between chemical cleaning), better TOC reduction, and as well, lower aluminium residual in the permeate (due to lower alum dosage).

The objectives of this study were of two fold:

1. To compare the performance of three low-pressure hollow-fibre water treatment membrane systems, and
2. To evaluate the effect of pretreatment with PAC and chemical coagulation on the performance of the three membrane systems.

10.2. MATERIALS AND METHODS

10.2.1. Raw Water

Raw water source for the entire study period was the Seymour reservoir located in North Vancouver, British Columbia. The water was characterized by low turbidity, colour and alkalinity. Table 10.1 summarizes raw water quality encountered during the study period.

Table 10.1Raw water characteristics at Seymour Reservoir.

Turbidity (NTU)	0.553 ± 0.451
UV_{254} absorbance (cm^{-1})	0.087 ± 0.018
TOC (mg/L)	2.43 ± 0.827
pH	5.80 to 6.90
Temperature (^{o}C)	3.0 to 14.0
Particles Count, 2 to 15 μm (particles/mL)	430 to 3500

10.2.2. Pilot Plant Description

The performance of three different low-pressure membrane pilot units was evaluated during the study. The first unit (membrane A), operated between March and July 2000, was a hydrophilic immersed UF membrane. Membranes B and C, which were operated between September 2000 and February 2001, were MF and UF pressure units, respectively. Selected manufacturers' specifications for the three membrane systems are summarized in Table 10.2.

Table 10.2 Manufacturer specifications for three membrane modules used during pilot study.

	Membrane A[†]	**Membrane B**[‡]	**Membrane C**[*]
Active area	60 m^2	45 m^2	7.2 m^2
MWC (Daltons)	~100 K to 120 K	NA	100 K
Pore size (μm)	0.035	0.2	0.01
Membrane process	Ultrafiltration	Microfiltration	Ultrafiltration
Membrane configuration	Immersed	Pressure type	Pressure type
Membrane material	NA	Polypropylene	Cellulose acetate
Hydrophobicity	Hydrophilic	Hydrophilic	Hydrophilic
Operating pressure (kPa)	-7 to -83	103 to 240	47 to 150
Design flux ($L/m^2 \cdot hr$)	51 to 102	not available	not available
Flow direction	Outside in	Outside in	Inside out
Mode of operation	Crossflow	Dead-end	Dead-end/Crossflow
pH range	5 to 9	NA	4 to 8.5
Chlorine tolerance (mg/L)	< 1000	No tolerance	< 100

[†] Zenon ZeeWeed [‡] US Filter/Memcor [*] Aquasource

NA: not available

10.2.3. Analytical Methods

Turbidities of raw water as well as permeate from the three pilot units were determined using both online (Hach 1720C) and bench-scale (Hach 2100N) turbidimeters.

The absorbance of ultraviolet light, at a wavelength of 254 nm, was measured daily using a Milton Roy Spectronic 21 spectrophotometer for raw water and permeate samples from all three pilot units. All measurements were performed in triplicates.

Online particle measurement was conducted for raw water and permeate samples using Met One Model 215W particle counters. In addition, daily grab samples of raw water and permeate were analyzed for particles in the range of 2 to 100 μm using a bench-scale particle counter.

Non-purgeable total and dissolved organic carbon (TOC, DOC) were measured using a SchimadzuTOC-5000A at the laboratories of University of Alberta. Samples were preserved at pH of 2 and stored at 4°C for no longer than 21 days. Other daily analysis and measurements included pH, temperature, feed, permeate and reject pressures, and feed and permeate flow rates.

10.2.4. Pilot Plant Operation

To establish the optimum flux, all three membrane pilot units were initially operated at three different flow rates in accordance with the manufacturer's recommendations. Each membrane run was performed for five to seven days or until the maximum allowable transmembrane pressure (TMP) was reached. Most runs were performed at recovery rates of 95% to 99%. To overcome reversible fouling, all three membrane units incorporated regular backwashing cycles. In addition to backwash cycles of 15-seconds duration and 15 to 30-minute frequencies, membrane A also utilized continuous or intermittent aeration using coarse bubble diffusers located at the bottom of the module. Membrane B utilized air pressure in the reverse direction followed by a water rinse once every 22 minutes. Membrane C utilized permeate at high pressure flowing in a reverse direction at 29-minute intervals. All three membranes were operated at constant flux and variable TMP. The membrane pilot units were equipped with programmable logic controller (PLC) that was used for controlling the sequence of operation and for logging data. At the termination of each run, chemical cleaning was initiated for each membrane pilot unit using chemicals recommended by the manufacturers. The purpose of chemical cleaning was to restore TMP as close as possible to that of a new membrane.

10.3. RESULTS AND DISCUSSION

10.3.1. Performance Comparison

Two main criteria were established at the beginning of the study for comparing the performance of the membrane systems; 1) finished water quality, and 2) membrane's specific flux. Finished water quality was determined based on turbidity, UV absorbance (at 254 nm), and particle counts in the permeate. To provide a meaningful comparison between the membrane systems specific flux (also known as permeability) was used in place of TMP. The specific flux is the ratio of permeate flux (usually at 20°C) to TMP and is determined as given in Equation 1:

$$J_{sp} = \frac{J_{20}}{P_{tm}} \qquad [1]$$

where J_{sp} is the specific flux ($Lm^{-2}h^{-1}kPa^{-1}$), J_{20} is the permeate flux corrected for 20°C

($Lm^{-2}h^{-1}$) and P_{tm} is the TMP (kPa). Permeate flux was corrected for temperature effects using Equation 2 (Jacangelo et al, 1994):

$$J_{20^\circ C} = \frac{Q_p x e^{-0.0239x(T-20)}}{S} \qquad [2]$$

where: Qp is the permeate flow (L/h), T is the fluid temperature (°C) and S is the membrane surface area (m^2).

However, Karimi et al. (1999) suggested that Equation [2] may introduce an error of about 3 to 10 percent within the temperature range of 0 to 10 °C. They recommended the use of Equations 3 and 4 to correct for the effects of temperature on water viscosity.

$$\text{(For T} \leq 20\ ^\circ\text{C)}\ \mu_T = e^{-0.0282(T-20)} \qquad [3]$$

(For T > 20 °C) $\mu_T = e^{-0.021(T-20)}$ [4]

where μ_T is the water viscosity at the test temperature (T). The authors claimed that the above Equations produced much better estimates of water viscosities at various temperatures with en error of less than 2 percent. For the purpose of this project, the Equations proposed by Karimi et al. (1999) were used to account for the effect of temperature on water viscosity and permeate flux for all three membranes.

10.3.2. Finished water quality

Permeate quality for all three membranes was far better than the requirements set by the Canadian Drinking Water Guidelines (CDWQG). Finished water turbidities of less than 0.05 NTU were consistently produced by all three membranes. Particle counts (in the range of 2 to 15 μm) in the permeate were consistently less than two particles/mL, except immediately following backwash. Reduction in UV absorbance was, in most cases, insignificant for membranes A and B (less than 12%) but higher for membrane C (16% ± 6%) This was expected, since membranes A and B had larger nominal pore sizes (0.035 μm and 0.2 μm, respectively) as compared with membrane C (0.01μm) and can only reject insignificant amount of dissolved organic matter that contribute to UV absorbance at the wavelength of 254 nm. These results clearly indicate that finished water quality cannot be used to adequately compare the performance of these membranes, since all three membranes produced exceptional finished water quality. Other parameters, such as the specific flux, may prove to be a more effective parameter for comparing the performance of the membranes.

10.3.3. Specific flux

Figure 10.1 shows the specific flux profiles for the three membrane systems corrected to 20°C. As is demonstrated by Figure 10.1, membrane A shows the highest initial specific flux but after only 100 hours of operation, its specific flux drops below that of the membrane C. On the other hand, although membrane C has a lower initial specific flux, it retains its specific flux with little change over the entire operation period. Membrane B starts with the lowest specific flux, which drops further during first 25 hours of operation and remains relatively constant thereafter. Based on Figure 10.1, if a relatively high and stable specific flux was the main criteria for selecting the appropriate membrane, one would have chosen membrane C.

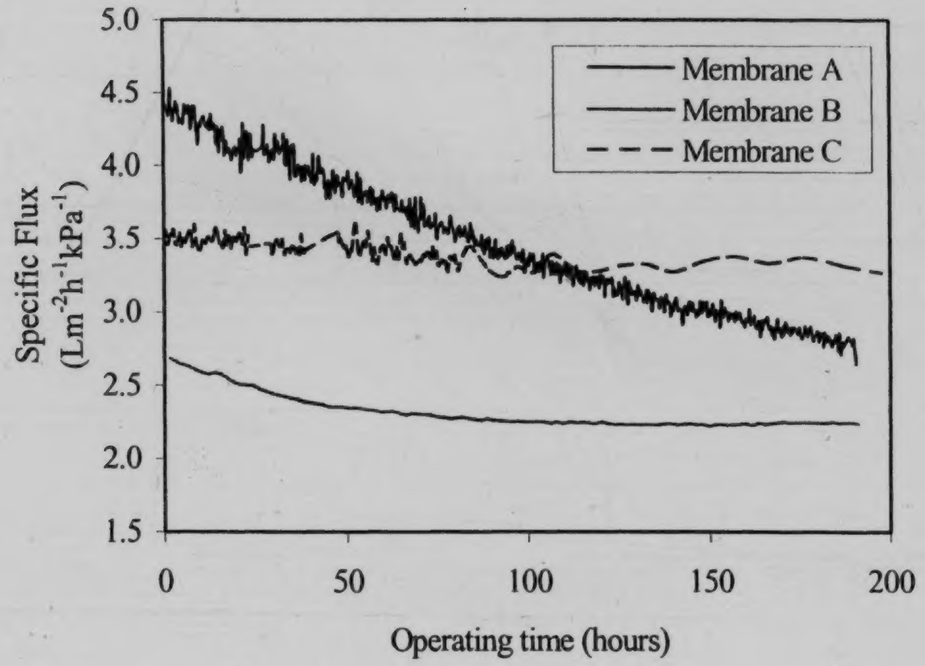


Figure 10.1 Specific flux profiles (corrected for 20°C) for three membrane pilot plants.

Figure10.1 also reveals some interesting points with respect to the mechanism of membrane fouling. The nominal pore size of membrane A (0.035 μm) is between those of membrane B (0.2 μm) and membrane C (0.01 μm). The dominant mechanism for fouling in membrane A appears to be pore plugging. It seems that the constituents of raw water responsible for membrane fouling are within the size range that is either too small or too large to cause pore plugging in membranes B and C, respectively. They, however, cause significant pore plugging in membrane A, reducing its specific flux to less than that of membrane C and close to that of membrane B. For membrane C with the lowest nominal pore size, the main mechanism for fouling may be attributed to cake layer formation that can be overcome largely by backwashing the membrane. For membrane B, the fouling mechanism may be a combination of pore plugging and cake layer formation. In addition, membrane A may have been more prone to adsorptive fouling which usually leads to either pore plugging or formation of a cake layer that is not easily removed during backwashing.

The rapid loss of permeability observed in membrane A, in relation to that of membrane C with lower initial permeability, had been observed previously. Dal-Cin et al. (1995) observed highest relative fouling with the most permeable membranes when exposed to the effluent from a plug screw feeder pressate from a semi-chemical mechanical pulp mill. They attributed this phenomenon largely to the occurrence of adsorptive fouling at the membrane surface and pores.

10.3.4. Feed Pre-treatment

The effect of feed pretreatment on the removal of disinfection byproducts (DBP) precursors and membrane performance (membrane fouling) was evaluated at this stage of the study. Powdered activated carbon (PAC) addition and chemical coagulation were performed during the pre-treatment study.

Two types of PAC were considered; ACTP from PrairieChem, Inc. and WPH from Calgon Corporation. Specifications for both types of PAC are summarized in Table 10.3.

Table 10.3 Specifications for PAC used during the pilot study

Specifications	ACTP	WPH
Iodine Number (mg/g.min.)	550	1052 to1074
Phenol Value (ppm)	16 to 20	NA
Modified Phenol Value	1.82 to 2.28	NA
Screen Analysis	90% through 325 mesh US	95% through 325 mesh US
Molasses No.	not available	251 to 253
Ash % by Weight	1.5	7.4 to 7.7
Moisture % by Weight	5%	2.5 to 2.6

A combination of granular alum (membrane A) or polyhydroxy aluminium chloride (PACl for membrane B) and soda ash (for pH and alkalinity control) was used during the coagulation pre-treatment. PACl was used at the request of the manufacturer for membrane B. Due to shortage of time, other coagulants such as ferric chloride were not evaluated during this study. Mixing for coagulation was provided either through aeration in a mixing tank (provided by manufacturer of membrane A) or by an inline static mixer (membrane B). The coagulated raw water was directly fed to each membrane without settling.

Chemical coagulation was only performed on membranes A and B as the manufacturer of membrane C did not allow the use of a chemical coagulant with its membrane. For the similar reason, PAC was not used with membrane B. Table 10.4 summarizes the pretreatment procedure during this study.

Table 10.4 Summary of pretreatment runs during the pilot study.

	Membrane A	Membrane B	Membrane C
PAC (mg/L)	15 and 20	NA	5, 10, 15, 20
Alum‡(mg/L)	4 and 10	NA	NA
PACl‡(mg/L)	NA	2, 4, and 8	NA

‡ pH was maintained between 5.9 and 6.2.

NA: not applicable

Prior to conducting the pretreatment trials, jar testing was performed with coagulants and PAC to determine the optimum dosage and conditions for pretreatment. Jar testing for both PAC and coagulants was conducted in a standard Phipps and Bird jar testing equipment with 2-L gator jars. Jar tests were conducted at various PAC and coagulant concentrations and impact on UV absorbance of the effluent was evaluated for each test. The jar test results indicated that the WPH PAC was more effective in reducing UV_{254} absorbance than the ACTP PAC. A previous study on Pac/UF on a different water source had also determined the WPH PAC to be a more suitable PAC for pretreatment with UF membranes (Jacangelo et al. 1994). PAC and coagulant dosages were determined based on the removal of UV absorbance, results from previous work on this topic (Adham et al. 1991; Lee et al. 2000), manufacturer's recommendations as well as the results of jar tests. It should be noted, however, that the actual concentration of PAC and coagulant in the system far exceeds the dosage and is primarily a function of membrane recovery and backwashing frequency. Recovery for UF and MF membranes is defined as the ratio of permeate flow to the feed flow and, for most pretreatment experiments, the membrane pilot plants were operated at recoveries of 95%. The higher the recovery, the larger is the concentration of coagulant or PAC in the system. For this study, the actual concentration of pretreatment chemicals in the system was estimated to be as high as 400 mg/L for PAC and 200 mg/L for the coagulants.

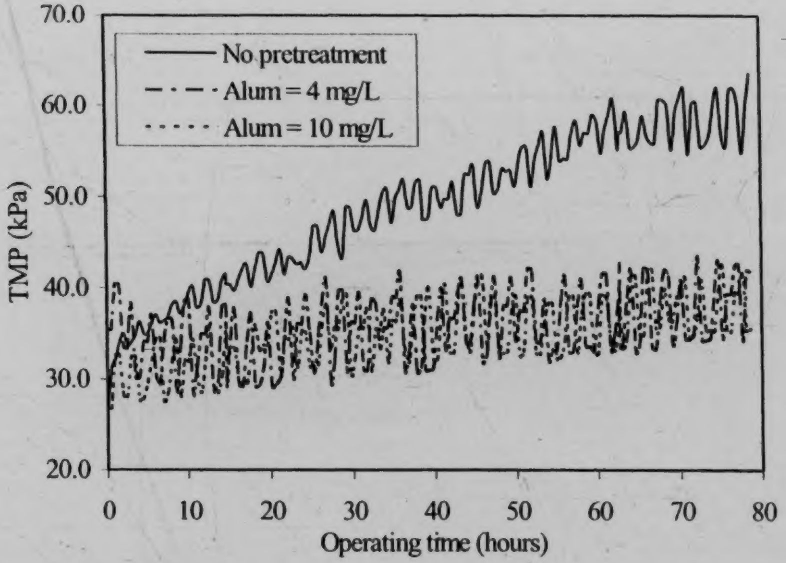
10.3.5. Removal of DPB precursors

The impact of pretreatment on the reduction of DBP precursors was evaluated at this stage of the study. Removal of DBP precursors was evaluated based on reductions in UV absorbance (UVA) and TOC in the permeate. Highest reductions in UVA (86.5%±3.4%) and TOC (57.5%±4.1%) were achieved with coagulation using PACl (8 mg/L). Coagulation with alum (10 mg/L) resulted in UVA and TOC reductions of 79.5%±3.8% and 54.0%±5.1%, respectively. Pretreatment with PAC did not yield significant reductions in UVA and TOC. PAC pretreatment resulted in 12.7% to 31.0% reduction in UVA and 6.2% to 35.4% reduction in TOC.

From the results obtained during the pretreatment trials, it appears that coagulation prior to UF or MF using either alum or PACl, is a more effective means for reducing the DBP precursors for the type of water treated during the study.

10.3.6. Impact of pretreatment on membrane fouling

The impact of pretreatment on the reversible fouling of membrane systems was evaluated at this stage of the study. Membrane fouling was represented by the rate of increase in TMP over time (at constant flux). Figures 10.2 to 10.4 show the effect of pretreatment on reversible fouling of the membranes during the study.



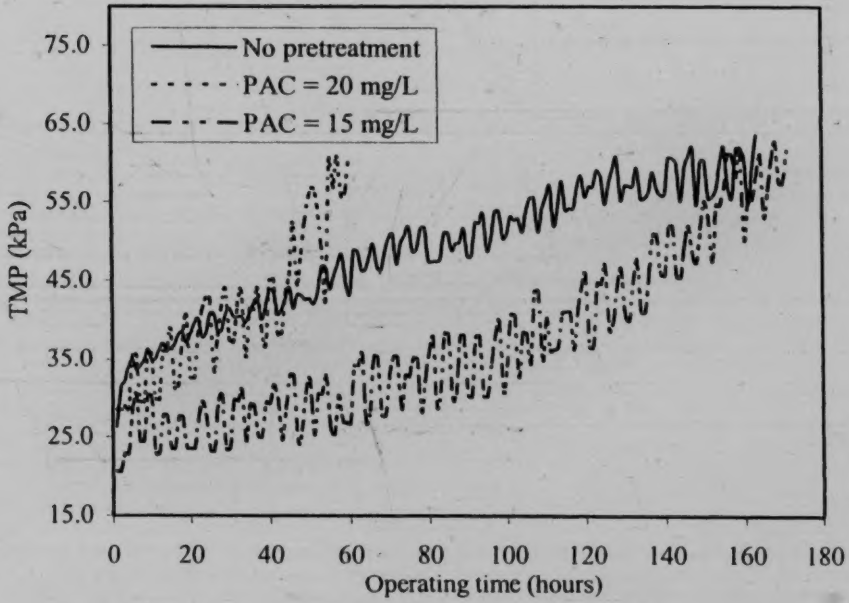


Figure 10.2 Impact of coagulation on reversible fouling in membrane A: a) coagulation, b) PAC addition.

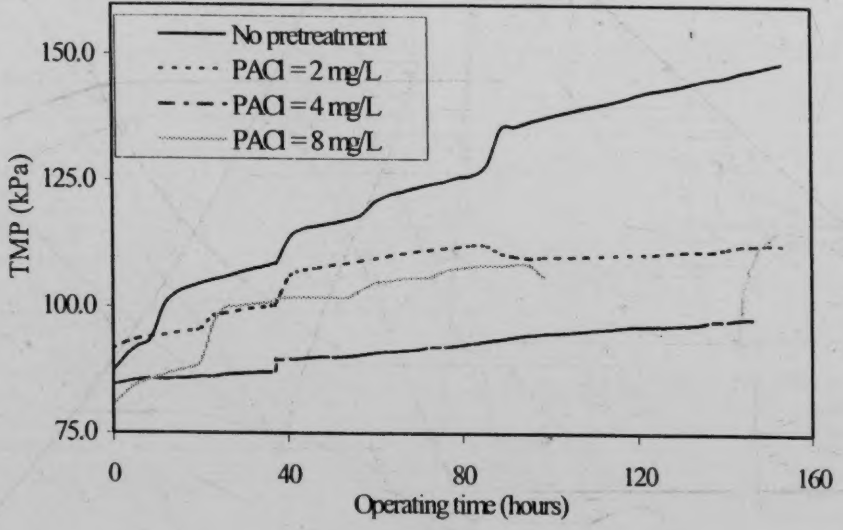


Figure 10.3 Impact of coagulation with PACl on reversible fouling in Membrane B.

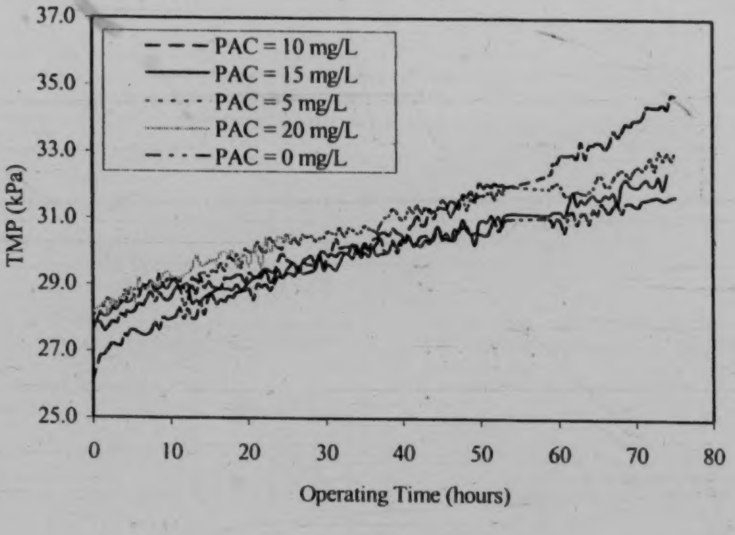


Figure 10.4 Impact of PAC addition on reversible fouling in membrane C.

It is evident from these figures that chemical coagulation and PAC addition impact membrane fouling in different ways. Figures 10.2a and 10.3 clearly demonstrate that chemical coagulation resulted in significant reduction in the rate of reversible membrane fouling (increase of TMP over time). The rate of TMP increase over time was reduced by 3.5 times (at 10 mg/L of alum) to 5.2 times (at 4 mg/L of alum) for membrane A, and by 1.5 times (PACl at 8 mg/L) to 4.1 times (PACl at 4 mg/L) for membrane B following chemical coagulation. These findings are in agreement with those reported by most other researchers on the effect of coagulation on the rate of membrane reversible fouling (Best et al. 1999; Lee et al. 2000). In contrast, PAC addition seems to have increased the rate of membrane fouling for membrane A and C under all PAC concentrations. The most drastic increase in membrane fouling was observed with the addition of 20 mg/L of PAC in the feed to the membrane A. The increase in TMP under this condition appears to be exponential, increasing relatively slowly at first and quite rapidly towards the end of operating cycle. Similar exponential increase in TMP over time occurs with PAC addition at 15 mg/L (membrane A) but not as severely. The impact of PAC addition on the rate of reversible fouling in membrane C is not as significant as that for membrane A. Under all dosing conditions, however, PAC seems to have increased the rate of membrane fouling when compared with the run with no pretreatment (PAC = 0 mg/L). Most of the previous work on PAC addition with UF has reported a decrease in the rate of membrane reversible fouling, with consequent increase in filtration runs (Adham et al. 1991; Campos et al. 2000; Snoeyink et al. 2000).

Several reasons have been suggested for the mechanisms by which coagulation reduces the rate of membrane fouling. These include reduced pore penetration (pore plugging), increase in porosity of the cake layer formed on the surface of the membrane, and enhancement of the rate of backtransport of particles due to increase in overall particle size as the result of coagulation (Wiesner and Laine 1996). Figure 10.5 shows the pattern of TMP recovery following each automatic backwash in the membrane A with and without coagulation. Two important observations can be made from Figure 10.5. The first observation is that backwashing effectiveness in recovering TMP pressure in membrane A was significantly higher for coagulation than with no coagulation. This is especially true at beginning of filtration runs, where TMP recoveries increased as much as six times with coagulation (4 mg/L of alum). This implies that coagulation produced a cake layer that showed less resistance to backwash than that produced without coagulation. Increase in particle size following coagulation was, most likely, the main reason for this phenomenon. This clearly indicates that reduction in the rate of membrane fouling with coagulation pretreatment resulted from increase in the effectiveness of backwash rather than higher permeability of the cake layer. Figure 10.5 points to another interesting phenomenon. The rate of TMP recovery remained relatively constant under coagulation pretreatment throughout the filtration run. This is, however, not the case for the run without coagulation, where the TMP recoveries increased over time to those observed with coagulation at higher alum dosage (10 mg/L). This may be explained as follows. As discussed earlier, the dominant mechanism for fouling in membrane A was pore plugging (adsorption of small particles on the membrane pores). Backwashing is not as effective in removing particles from membrane pores as is in removing the cake layer from the membrane surface. Therefore, lower TMP recoveries are observed at the beginning of filtration cycle without pretreatment. After some time, however, cake layer formation becomes the dominating mechanism for fouling and relative recoveries of TMP increases following backwash. Under coagulation conditions, pore plugging was minimized, resulting in higher TMP recoveries throughout the membrane run.

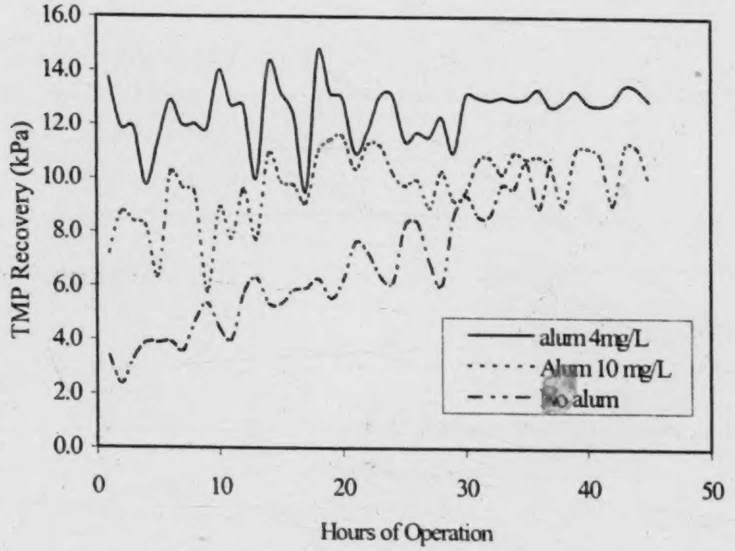


Figure 10.5 Impact of coagulation on the recovery of TMP following membrane backwash (membrane A).

Results from coagulation runs reveal another important point. For both membranes A and B and using either coagulant (alum and PACl), rate of membrane fouling was lower at lower coagulant dosage of 2 and 4 mg/L as compared with coagulant dosages of 8 and 10 mg/L. This is in agreement with the result of the work performed by Lee et al. (2000), who showed coagulation had its best effects with respect to membrane fouling at coagulation conditions corresponding to charge neutralization (low coagulant dosage and optimum pH). They showed that coagulation at higher coagulant doses, corresponding to sweep coagulation, did not result in noticeable improvements in TMP and in some cases resulted in higher fouling rates. For membrane B, the highest reductions in the rate of membrane fouling resulted from coagulation at PACl dose of 4 mg/L.

Although only alum and PACl were used during this study, pretreatment with other chemical coagulants, such as ferric chloride, has also been shown to reduce the rate and extent of membrane fouling (Schimmoller et al. 2001).

It is more difficult to explain the negative impact of PAC on membrane fouling. Most researchers agree that the impact of pretreatment on membrane fouling is a strong function of raw water characteristics including the nature of DOM and raw water chemistry as well as membrane's surface chemistry. Takizawa et al. (2000) evaluated the kinetics of contaminant removal and membrane fouling in a PAC-MF system. They showed that, in waters high in colloids, PAC addition resulted in higher rates of membrane fouling. They hypothesized that PAC particles contributed to the formation of a cake layer with much lower permeability (higher resistance) by bridging the colloids on the membrane surface. This phenomenon may explain the higher fouling rates observed with PAC addition during this pilot study. However, further detailed studies are required to adequately identify the factors that contribute to increased rate of membrane fouling during the PAC addition experiments. Findings of this study, with respect to the effect of PAC addition on the rate of membrane fouling, appear contrary to results from previous studies which were outlined earlier in this paper. This may indicate that the impact of PAC addition on the rate of membrane fouling is a strong function of raw water characteristics.

10.4. CONCLUSIONS

The following conclusions can be drawn from the results of this pilot study:

1. All membrane pilot systems consistently produced better quality water than recommended in the CDWQG with respect to turbidity and achieved greater than 3 log removal of particles in the range of 2 to 15 μm.

2. Specific flux provided an effective basis for comparing the performance of different types of membranes.

3. Chemical coagulation with alum and PACl resulted in relatively good removal of DBP precursors and significant reductions in the rate of membrane reversible fouling.

4. For the type of raw water used, PAC addition resulted in moderate reductions in DBP precursors but, in most cases, increased the rate of membrane fouling specially at higher dosages.

5. Chemical coagulation reduced the rate of membrane fouling by minimizing pore plugging and increasing the efficiency of membrane backwash.

6. The effectiveness of pretreatment prior to membrane filtration is a strong function of raw water characteristics and must be evaluated on a case-by-case basis.

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CHAPTER 11. GENERAL CONCLUSIONS AND RECOMMENDATIONS

11.1. GENERAL OVERVIEW

Low-pressure membranes, microfiltration (MF) and ultrafiltration (UF) are a proven technology for removal of many pathogenic organisms in water, including *Cryptosporidium* spp., *Giardia* spp. and bacteria. The high degree of microbial removal achieved by MF and UF membranes has given impetus to their rapid growth in the water treatment industry. Two outstanding issues with regards to microbial removal ability of MF and UF membranes still remain. The first is the development of a comprehensive membrane integrity monitoring program, which includes one or several membrane integrity tests. The second issue involves the reported inconsistencies of MF membranes in virus removal. The United States Environmental Protection Agency (USEPA) is proposing to include regular direct integrity monitoring tests as a requirement for all membrane water treatment plants. To receive credits for *Cryptosporidium* spp. removal, these direct integrity monitoring tests should be able to detect small breaches in membrane integrity (resolution), should be able to closely predict log removal values (sensitivity), and must be performed on a daily basis (frequency). The proposed Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) allows either pressure-based integrity monitoring tests (pressure decay tests, diffusive air flow test) or marker-based tests (latex beads, molecular markers, etc.), as long as these tests have the sufficient resolution and their sensitivity has been verified through challenge testing. In terms of virus removal, only two U.S. states grant MF membrane any virus removal credits (0.5 logs) due mainly to their inconsistency in removing viruses. Since the primary drive for the growth of MF and UF membranes has been, and will continue to be, their ability to reject many pathogens of interest to the water treatment industry, it is important to address the two outstanding issues of membrane integrity monitoring and virus removal efficacy of MF membranes.

The main scope of this research project was, therefore, of two fold:

1. to enhance the integrity monitoring of low-pressure membranes by either improving the current direct integrity monitoring tests or by developing new tests; and
2. to investigate the mechanisms for virus removal by MNF membranes and to identify conditions for optimum rejection of viruses by MF membranes.

An extensive review of current integrity monitoring tests revealed several deficiencies with respect to pressure-based membrane integrity monitoring tests. These deficiencies included, among others, lack of resolution to detect minor breaches of membrane integrity for large membrane plants, the potential for variability of test results under varying operating conditions especially water temperature and membrane fouling, and lack of sensitivity to accurately predict log removal values (LRV) of *Cryptosporidium* spp. based on the results from the pressure-based integrity monitoring tests. For pressure-based integrity monitoring tests, such as the pressure decay test, the loss of pressure was thought to be the result of either air diffusion through wetted intact pores, or bulk flow of air through a defect. For membranes, with large surface areas, pressure decay due to a small integrity breach is often masked by the larger decay due to air diffusion. Therefore, estimating and accounting for the contribution of air diffusion to pressure decay would result in increased resolution of the pressure decay test.

Another important consideration that had not been previously addressed is the effect of water temperature on the pressure decay test. Water temperature affects its surface tension, contact angle and viscosity, as well as the diffusivity constant and solubility of air in water. All of these parameters may impact the rate of air diffusion through intact membranes. At very low water temperatures, lower pressure decay rates caused by the drop in the rate of air diffusion, may produce false negative results. The opposite may also be true for very warm surface waters. Such false negatives or positives in turn will adversely impact the resolution of pressure decay tests. The extent of membrane fouling may also impact the rate of air diffusion and consequently the result of the pressure decay test. As the pores of the membrane are constricted by foulants and with increased resistance and lower porosity caused by the fouling layer, the diffusion rate is also expected to drop. Finally, since immersed membranes conduct the pressure decay test while the membrane is submerged, the impact of submergence on the rate of diffusion and hence pressure decay must be evaluated.

The sensitivity of the pressure decay test, its ability to correlate with LRV, should be established for low-pressure membranes. Although some attempts have been made in the past to determine the sensitivity of pressure decay test for the ZW1000$^{\copyright}$ or ZW500d$^{\copyright}$, no comprehensive challenge test had been previously performed with these membranes. Furthermore, the reliability of the existing theoretical relationships for estimating LRV based on the pressure decay test results had to be verified.

Since challenge testing of membranes with biological surrogates, such as bacterial spores, is often very expensive, cumbersome and time consuming, identification and evaluation of alternative non-biological surrogates for challenge testing of membranes was of outmost important. In this context, fluorescent latex microspheres offer distinctive advantages over biological surrogates in terms of simplicity, cost and time requirements. Several outstanding issues with respect to the use of latex microspheres had to be resolved, including the optimum size, charge, and the most effective method(s) of enumeration.

In terms of virus rejection ability of MF membranes, one important issue was to determine the mechanism of virus removal under pilot-scale operations. Such work had been previously performed on lab-scale modules, but no comprehensive work for pilot-scale systems was available. Laboratory studies previously examined one mechanism at a time, such as adsorption or fouling, for very short durations. A pilot-scale study would allow evaluation of both mechanisms under long-term operations.

Once mechanisms of virus removal for long-term operation of MF membranes had been identified, attempts were made to determine conditions to optimize the effect of these mechanisms. Adsorption was identified as an important mechanism for a clean membrane and, therefore, attempts were made to optimize adsorption under different water chemistry conditions and using chemical coagulation.

Finally, the impact of chemical coagulation on the performance of MF and UF membranes was evaluated. The intent was to determine if chemical coagulation would detrimentally impact the membrane or it would enhance its performance by reducing the rate of membrane fouling.

11.2. CONCLUSIONS

The results of this research project has helped enhance the efficacy of low-pressure membranes, especially the immersed membranes, by not only providing valuable insights into the fundamental processes responsible for removal of microorganisms but also by developing means for improving both the microorganism removal and the process of monitoring the extent of such removal. The most significant findings of this research projects are summarized below.

11.2.1. Direct Integrity Monitoring Tests

1. Using the Fick's first law of diffusion, it was shown that pressure decay measured for an intact membrane is primarily due to the diffusion of air through the wetted pores. The estimated pressure decay can act as a baseline for interpreting the pressure decay results for the ZW500d© membrane.

2. To reliably estimate the rate of diffusion of air through an intact membrane, the Fick's first law of diffusion was modified by the addition of a new parameter called the membrane parameter (κ). The membrane parameter which has a unit of m^{-1}, is unique to the specific membrane, and describes the effect of pore's tortuosity, porosity, and effective diffusion length on the rate of air diffusion through the intact membrane. The membrane parameter must be determined experimentally for a specific membrane system.

3. Using the newly developed membrane parameter, in conjunction with the Fick's first law of diffusion, allowed for relatively accurate prediction of diffusive air flow rates and pressure decay rates for the ZW500d© with different surface area. Estimating the base pressure decay (pressure decay of an intact membrane) and subtracting it from the measured pressure decay will greatly improve the resolution of current pressure decay tests for the ZW500d© membrane.

4. Water temperature was found to have a considerable impact on the rate of air diffusion and hence pressure decay for an intact membrane. The impact was most noticeable at close to 0°C, when there was a decrease of about 42% in diffusive air flow rate and 44% in pressure decay rate.

5. An Arrhenius-type relationship was proposed to correct for the effect of temperature on the diffusive air flow rates. This relationship appeared to have a similar exponential decay term as the correction factor for the effect of temperature on membrane flux (viscosity effects) proposed by other researchers.

6. The extent of membrane fouling was found to have a noticeable impact of diffusive air flow rates. As the membrane was progressively fouled, both the rate of diffusive air flow and pressure decay rate decreased accordingly.

7. Under submerged conditions, diffusive air flow rates were substantially lower then those measured without submergence. The impact of submergence on the rate of diffusive air flows may be due to an increase in the effective diffusion length of the intact membrane. It was also suggested that a geometric average would better represent the effective submergence depth, than an arithmetic mean.

8. An extensive challenge testing of ZW1000© and ZW500d© pilot units was performed using *Bacillus megaterium* spores as surrogates for *Cryptosporidium* spp. The results indicated that both membrane pilot plants consistently achieved greater than 7 log removal of spores under intact conditions. Removal of spores decreased, however, as the membranes were compromised increasingly. The sharpest drop in LRV for the ZW1000© pilot plat was observed after the introduction of one pinhole while the steepest drop in LRV for the ZW500d© unit occurred after cutting one fibre. This highlights the impact of the fibre's inside diameter on LRV of compromised membrane, as the ZW500d© fibre has an inside diameter of over two times that of the ZW1000© fibre.

9. The rate of drop in the LRV for increasingly compromised membranes exhibited an exponential decay trend, indicating that the reduction in LRV with increasing number of defects is not cumulative. It was concluded from the results of the challenge study that, even under sever compromised conditions (over 218 broken fibres in a 1 MLD plant), the LRV of the membranes tested will not drop below 3 logs.

10. Backpulsing appears to affect the LRV of the membrane differently depending on the type of defect. Backpulsing with the presence of one or two pinholes resulted in a large drop in LRV, as compared with backpulsing an intact membrane or a membrane with broken fibres. It was suggested that

backpulsing may enhance the effect of pinholes by either increasing the size of the hole temporarily or by unplugging an otherwise plugged hole.

11. It was also concluded that bacterial spores may not be the most suitable surrogates for membrane challenge tests, due to the difficulty and cost of production, and labour extensive and costly enumeration procedures. Other alternative, non-biological surrogates should be identified and evaluated as candidates for membrane challenge studies.

12. The application of latex microspheres as non-biological surrogates for challenge testing, as well as occasional direct integrity monitoring of low-pressure membranes, was also evaluated. It was concluded that the size of microspheres is the most important factor and not the microsphere's charge (i.e. presence of different functional groups). Carboxylated latex beads, with yellow green or yellow orange fluorescent dyes and 0.5 μm diameter, were selected as most suitable for membrane challenge testing.

13. Of all methods evaluated for enumeration of water samples containing latex beads (flow cytometry, hamocytometry, fluorometry, and confocal microscopy), use of confocal laser scanning microscopy was found to be most suitable for enumerating samples with very low bead concentrations such as the permeate from an intact membrane. Hemacytometry can also be used for enumeration of samples with high bead counts. Use of latex microspheres, if

found feasible, would be a considerably more cost effective method for challenge testing of membranes, compared to biological surrogates such as bacterial spores.

11.2.2. Rejection of Viruses by Microfiltration Membranes

1. The removal of viruses by MF membranes was evaluated using bacteriophages native to secondary effluent as surrogates. The removal of bacteriophages increased substantially after the first 20 hours of operation and remained more or less constant thereafter.

2. Two distinct mechanisms for rejection of bacteriophages by MF membranes were suggested. The dominant mechanism for the initial removal of bacteriophages was adsorption of bacteriophages on the pores and surface of the membrane. This mechanism dominated only for the short period, when the membrane was clean. As the MF operation continued beyond the first few hours, fouling became the dominant mechanism for removal of bacteriophages.

3. Although membrane fouling is considered a detriment to membrane operation, in the context of virus removal however, fouling may be quite beneficial. It would be worthwhile to attempt to balance the negative and

positive consequences of membrane fouling for the most optimum operation of MF membranes in terms of flux as well as effluent quality.

4. The impact of permeate flux and transmembrane pressure (TMP) on the removal of bacteriophages was also evaluated. Increasing permeate flux or TMP was found to impact bacteriophage removal in two different ways depending on the extent of membrane fouling. The observed impact of permeate flux was yet another proof of the two distinct mechanisms for the rejection of bacteriophages by MF membranes. When the membrane was clean and adsorption was the dominant mechanism, increasing the permeate flux decreased the rejection of bacteriophages by MF membrane, most likely due to decreased adsorption caused by lower residence times. With the fouled membrane, bacteriophage removal increased initially with increasing permeate flux but dropped when permeate flux increased beyond a certain value. It was proposed that the initial increase in bacteriophage rejection was the result of increased resistance of the fouling layer as it became compressed. Above a certain permeate flux, increased shear forces dislodge the already captured bacteriophages and release them in the permeate.

5. Based on the above results it was proposed that the reported inconsistencies in bacteriophage removal by MF membranes may have been the result of sampling at different periods of operation. Sampling at initial stages of operation would most likely produce low LRV data, while sampling when the

membrane is fouled would result in higher reported bacteriophage rejection. It is also possible that varying water chemistry conditions resulted in different degrees of adsorption and hence different rates of bacteriophage rejection.

6. On the basis of the above findings, it was concluded that, to ensure consistent bacteriophage (and hence virus) removal by MF membranes, more attention should be paid to enhancing adsorption to increase bacteriophage rejection of the clean membrane. Conditions that improving adsorption, such as optimum water chemistry or chemical coagulation, should be further investigated.

7. The impact of pH and concentration of monovalent and divalent ions on the rejection of MS2 phages by MF membranes was investigated. It was observed that solution pH has a noticeable impact on the survival of MS2 phage. Varying degrees of MS2 phage inactivation was observed at different pH values, with the lowest inactivation around the neutral pH. It is not clear if such inactivation is permanent or temporary. The effect of pH on inactivation of MS2 may have important implications on conducting challenge studies with bacteriophages. It is important to always measure the concentration of phages after pH adjustment.

8. Another important factor that was observed during the study is the strong tendency of MS2 phage to adsorb on solid surfaces. In fact, much of MS2 phage rejection by the MF membrane, even at the isoelectric point of MS2,

could be attributed to adsorption to other surfaces than the membrane filter. It is therefore prudent to monitor and account for MS2 adsorption to other surfaces while conducting challenge testing of membranes with MS2 or other phages.

9. Chemical coagulation using alum appeared to have a positive impact on the rate of MS2 phage rejection by a MF membrane. Log removal of MS2 phage increased to over 1 at alum dose of 6 mg/L, but remained relatively unchanged thereafter with increasing coagulant dose.

10. Finally, chemical coagulation is not only beneficial for enhancing the efficacy of MF membranes for virus removal, it also helps to significantly improve the performance of low-pressure membranes by retarding or reducing the rate of reversible membrane fouling. Alum, at relatively low concentrations (less than 10 mg/L), proved to be very effective in prolonging membrane runs prior to chemical cleaning. It should, however, be noted that the impact of chemical coagulation or other chemical and physical pre-treatment on the performance of membrane depends on raw water characteristics and must be evaluated on the case by case basis.

11.3. RECOMMENDATIONS

This research project provided answers to several outstanding issues with respect to direct membrane integrity tests and virus removal efficiency of MF membranes.

Results obtained from this research project can be used to achieve at least two objectives: to improve the microbial removal efficacy of low-pressure membranes, and to plan further research in this area. Towards achieving the first objectives, the following recommendations are offered:

1. A comprehensive membrane integrity program should be devised which incorporates several different integrity monitoring tests and which provides standard procedures for conducting and interpreting the results of such tests.

2. All membrane manufacturers should attempt to develop theoretical relationships for estimating the contribution of diffusion to pressure decay or diffusive air flow tests for their respective membranes, to enhance the resolution of their direct integrity testing and improve their sensitivity.

3. When conducting pressure-based membrane integrity tests, the impact of water temperature must be fully considered and incorporated in the results.

4. To improve the efficiency of MF membranes for virus removal, chemical or physical pre-treatment steps should precede low-pressure membranes. This would not only enhance virus removal, but also could greatly improve the performance of MF membrane by lowering the rate of membrane fouling and improving water quality by removing natural or synthetic organic carbon compounds.

The following recommendations are offered towards future research in the area of membrane integrity monitoring and virus rejection by MF membranes:

1. The impact of membrane fouling on the rate of air diffusion and pressure decay should be further investigated under pilot or full-scale operating conditions.

2. The impact of submergence on the pressure decay testing of immersed membranes should be further evaluated and incorporated in the existing model for estimating the contribution of diffusion to pressure decay.

3. The feasibility of latex microspheres as surrogates for *Cryptosporidium* spp. in membrane challenge testing should be further investigated. Use of confocal microscopy or another suitable enumeration technique should also be further developed.

4. The impact of pH on inactivation of bacteriophages should be studied in detail. It should also be determined if such inactivation is permanent or temporary.

5. The impact of water chemistry and physical and chemical pre-treatment on virus removal should be further studied.

6. The effect of feed particulate matter on the removal of MS2 phage by MF membranes with and without coagulation should be further studies.

APPENDIX A. INSTRUCTIONS FOR CONSTRUCTION OF BENCH-SCALE HOLLOW-FIBRE MEMBRANES

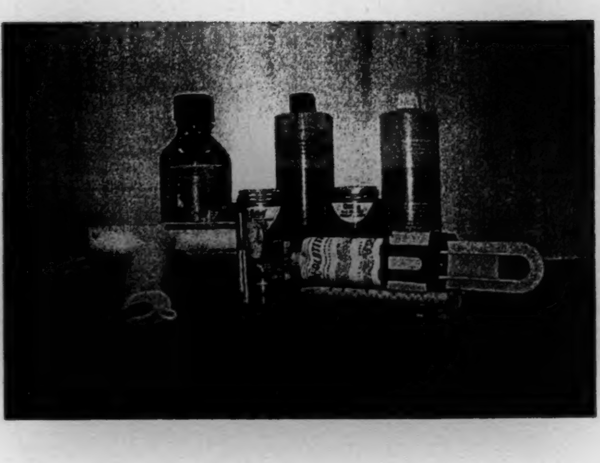
PROCEDURE FOR MAKING A MEMBRANE

Materials

The materials needed for constructing a hollow fiber membrane reactor include:

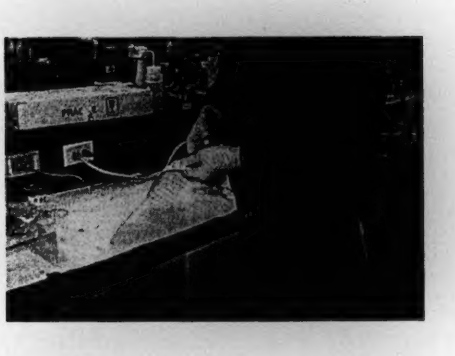
- Clear PVC pipe
- Top and bottom fittings
- ¼" plastic tubing
- Hollow fiber membranes
- Meshed fabric (with 1mm x 1mm openings)
- Teflon tape

- Various epoxies (listed throughout the document)
- Hot glue (glue gun)
- Glycerin
- Drill bit

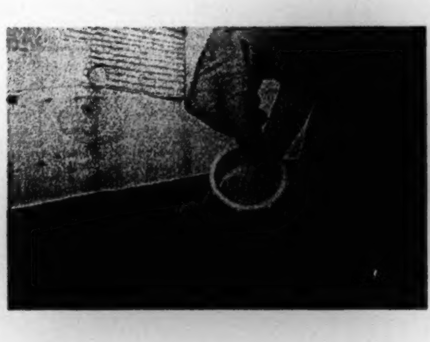


Preparing Fitting

1. Cut fabric to fit the size of the fitting chosen



2. Using the epoxy glue gun[1] and a static mixer applicator, glue the fabric onto the ledge in the fitting. Quickly clean off any excess epoxy.



When gluing in the fabric, make it as taught as possible and make sure there is a good seal around the edges. This will prevent epoxy from leaking through later in the process.

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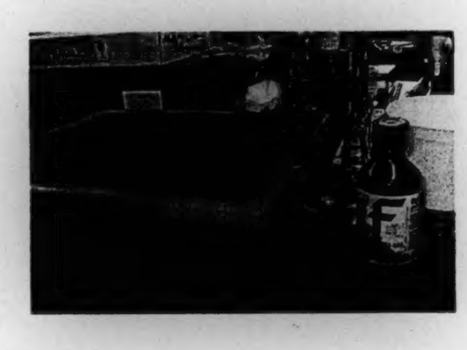
[1] 1500 PSI 15 minute epoxy from Holdtite Adhesive Canada Inc.

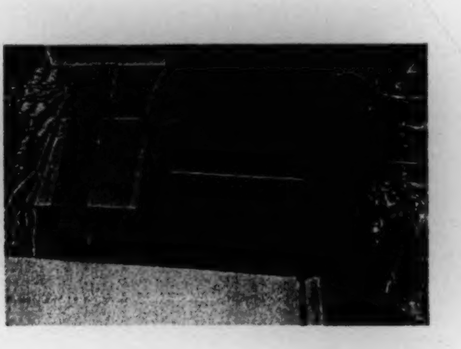
Preparing the Working Area

3. Prepare water – glycerin mixture in an appropriate container. Use approximately 50 mL of glycerin.



4. Wet lab bench with mixture

5. Measure out the desired length of fiber and create a template on the lab bench so that the length does not have to be measured for each fiber. The length of the fiber cut will not be the effective length as a portion of the fibers on the top and bottom will be sealed off by epoxy. Wear gloves when constructing the membrane so not to damage the fibers.

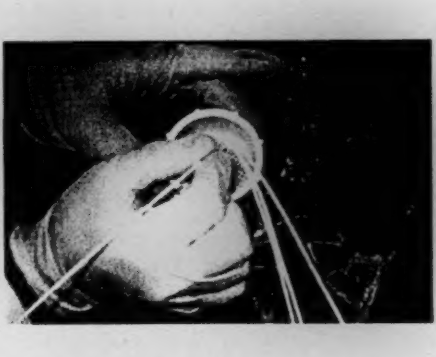


Constructing the Membrane

6. Cut the fibers at the measured length.

7. Place the cut fibers in the previously prepared water-glycerin mixture.

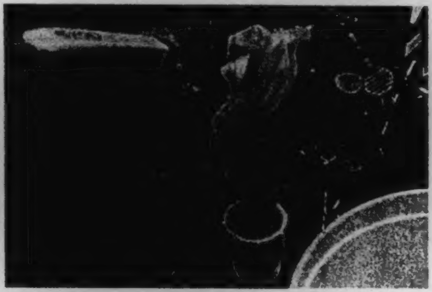
8. Thread the fibers through the openings in the fabric row by row. Count the number of fibers that are being used. Have the fitting sitting upright on the bench and push the fibers through until they hit the lab bench.



9. When complete, flip the membrane and ensure all fibers are of the appropriate length. Gently push the fibers another 2 cm past the bottom of the fitting

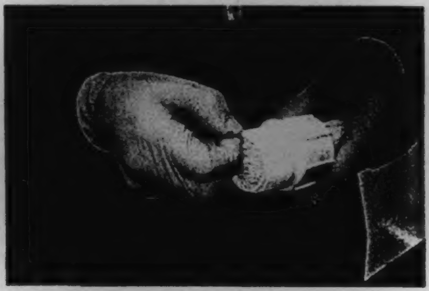
For the membrane shown on the right (1.25" dia.), approximately 100 fibers should be used and placed in the middle. This will make it easier to place the shell later in the process.

10. Set the partly constructed membrane in a bench clamp, having the clamp keep the fibers straight and upright. Use a glycerin-water soaked cloth to protect the fibers from the clamp.



Setting the Fibers

11. Using the epoxy glue gun and the static mixer applicator, place epoxy in the fitting at the base of the fibers. Ensure that the epoxy does not get on the fibers except at the base of the fitting. Let sit for 2 minutes, if the epoxy is successfully drying it should be turning yellow and giving off heat.



12. The epoxy should have encircled the fibers and the top of the fabric. Turn over the membrane and peel off (to the best of your ability) any epoxy that seeped through. This must be done before the epoxy completely dries. Cut off the protruding ends of the fibers so to make them flush with the bottom of the fitting.

13. Prepare a less viscous, two part epoxy[2] by mixing approximately 8mL of each the epoxy and the hardener together. This can be easily done by measuring equal volumes in test tubes first.

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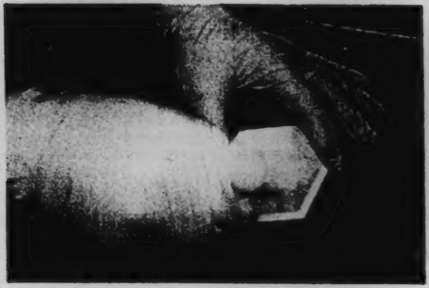
[2] One to one polymer coating containing epoxy bisphenol A resin



14. Mix for approximately two minutes before pouring on top of the first hardened layer of epoxy. Again, ensure not to get the epoxy on the fibers above placement. Pour a thin layer, leaving a half an inch to the top of the fitting for the sleeve that will be placed in the next stage of construction. Clean off excess epoxy from the fitting.

15. Wrap the fibers in glycerin-water wetted cloths so that they do not dry out. Be sure no to wet the cloth too much as no drips should fall on the epoxy. Another stand may be needed to hold the cloths in place.

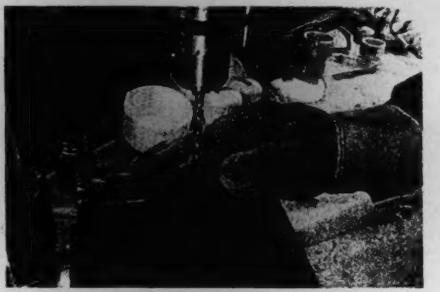
16. Let stand for 20 hours so the epoxy can fully harden.

Construction of the Sleeve

17. Using a spare fiber, measure the distance from the top of the epoxy to the end of the fibers. Cut a length of PVC pipe to this length.

18. Mark off two spots on the cut pipe above where the caps would go. The marks should be inline with one another and leave enough room above the top and bottom fitting for the ¼" tubing that will be used as spouts.

19. Using a drill press, drill through marks with a bit that matches the size of the plastic tubing that will be used.



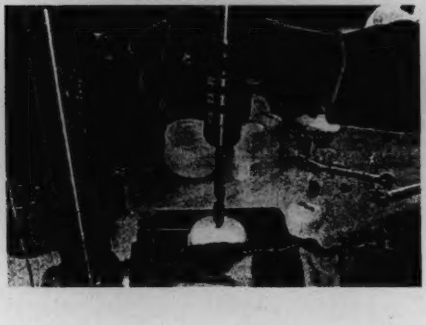
20. Thread the plastic tubing through the holes from the outside to the inside and push through until it protrudes out the end of the PVC pipe.

21. Heat a bit similar to the one shown with a Bunsen burner and push into the protruding tubing about 1 cm. The tubing should soften around the bit. Pull the bit away and press the hot end of the tubing flat against the lab bench to produce an open but flattened end.

22. From the outside of the PVC pipe, pull the tubing in and hot glue gun the inside flattened portion to the inside of the PVC pipe. Repeat for the other hole.

Construction of the Cap

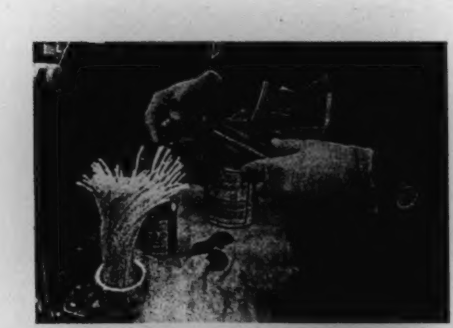
23. Drill a hole in the top of the threaded cap for the bottom fitting matching the size of the permeate piping.



24. Thread the hole and insert a threaded fitting. Use Teflon tape to seal the hole.

Assembly of the Filter

25. Brush the end of the PVC pipe with PVC primer (this can be messy so protect the working surface). Immediately after spread on the PVC cement[3], place over the fibers and insert into the fitting. Do this quickly and press down firmly and in a circular motion to ensure the pipe is inserted all of the way into the top cap.



26. Fill a small weighing dish with epoxy glue from the glue gun and tip the open tips of the fibers into the glue. This will seal the not permeate ends.

27. Fill the threadless cap half way with epoxy from the glue gun

28. Prime the bottom end of the PVC pipe, place the PVC glue on and slide into the epoxy filled bottom cap. Do this quickly and firmly so that the pipe goes all the way into the cap.

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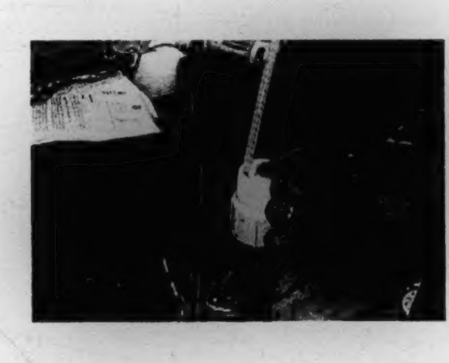
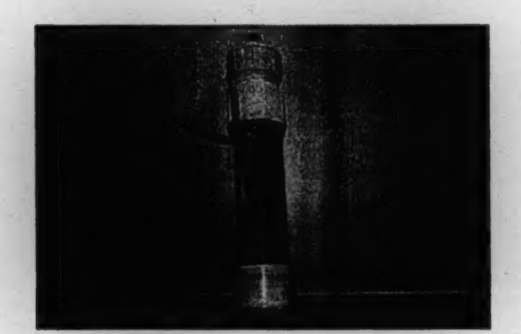
[3] Oatley PVC purple primer and heavy duty grey PVC solvent cement

29. Using the epoxy glue gun, fill the end with exposed fibers. Fill to approximately one centimeter below the top of the fibers.



30. Let all epoxy set for 20 hours.



31. Perform an integrity test on the new membrane.